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The first section of this report presents the basic concepts, mass balances (that applied to the water and that applied to the phosphorus), and force relationships.

The second section of this report concerns the quantification of total phosphorus input to Lake Erie from river basins and shoreline sources. A computational method called the Flow Interval Method was devised to permit the calculation of total phosphorus influx without measuring the total phosphorus concentration for the entire year.

Another important aspect of reducing total phosphorus influx from river basins is the understanding of the transport processes in rivers. The third section of this report concerns the transport of total phosphorus during storm events.

The fourth section of this report presents the derivation of the necessary equations used to calculate the distance of the travel density function from measurements of the water flow rate and the total phosphorus concentrations at a point in the stream.

A calculational technique used to analyze upstream point source inputs is presented in Section Five of this report.

PHOSPHORUS TRANSPORT IN RIVERS

by

FRANK H. VERHOFF
Department of Chemical Engineering
West Virginia University
Morgantown, WV   26505

DAVID A. MELFI
and
STEPHEN M. YAKSICH
Lake Erie Wastewater Management Study
U. S. Army Corps of Engineers
Buffalo, NY   14207

DAVID B. BAKER
Water Quality Laboratory
Heidelberg College
Tiffin, OH   44156

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SECTION II THE ESTIMATION OF NUTRIENT TRANSPORT IN RIVERS

A = Drainage basin area above a gaging station in square miles.

a_i = Arbitrary Constant

C_{TP} = Total phosphorus concentration on a given day in mg/l as P.

D = Total number of days in a given time period.

d_i = The number of days in a given time interval in which the flow rate was in the "i" interval.

F_A = Average of the four previous days daily averaged flows in cfs.

i = "i" interval

j = "j" point in "i" interval

k_i = Number of data points in the "i" interval.

k_r = Factor for r percent confidence interval based upon the normal distribution with mean zero and minus one.

L = Flux values for the "k" data point in the "i" interval.

L_{ij} = Flux values for the "k" data point in the "i" interval.

$\overline{L}$ = Average daily total phosphorus flux for a given time period.

$\overline{L}_i$ = Average total phosphorus flux for interval "i" for a given time period.

n = Exponent power for the drainage basin area.

P = Total phosphorus concentration in mg/l as P.

P_i = Probability that flow occurs in the "i" interval during a given period of time.

P_L = Low total phosphorus concentration for a given stream in mg/l as P.

Q = Instantaneous flow at time P was measured in cfs.

LIST OF SYMBOLS (Cont'd)

Q = Length of each flow segment.

Q_i = Maximum instantaneous flow rates for the "i" interval.

$\overline{S}_i^2$ = Standard error for the mean for interval "i."

$\overline{S}_i$ = Variance

V = Variance for the estimated average daily flux.

$\propto$ = Y - intercept of the least square equation.

β = Slope of the least square equation.

SECTION III TOTAL PHOSPHORUS TRANSPORT DURING STORM EVENTS

A = stream discharge area ft^2 (m^2)
C = total phosphorus stream concentration, ppm (mg/l)
C_{in} = total phosphorus inflow concentration, ppm (mg/l)
f = function of A and defines Q
f = derivative of f
q = influx volume rate per axial distance, cfs/ft $(m^3/sec/m)$
Q = volumetric flow rate of the stream, cfs (m^3/sec)
t = time, sec
TP = total phosphorus concentration, ppm (mg/l)
u = velocity, ft/sec (m/sec)
x = axial variable, ft (m)
$\triangle$ = increment of
$\propto$ = proportionality constant

Subscripts

i = ith station in the numerical solution
j = jth time in the numerical solution

INTRODUCTION

The research work contained in this report concerns the transport of total phosphorous and orthophosphorus to Lake Erie. The various calculational techniques for analyzing data obtained from Lake Erie tributaries are presented. These calculations were developed to determine the source of the phosphorus and to quantify the input to the lake. The source and quantity of phosphorous must be determined if successful pollution abatement strategies are to be devised for Lake Erie.

Under Public Law 92-500 the U. S. Congress directed the Corps of Engineers to develop a management plan which would rehabilitate Lake Erie. The Buffalo District of the Corps was specifically assigned the task. Thus, the Lake Erie Wastewater Management Study was formed.

From its conception, the basic goal of the study has been to develop a management plan which would reduce or reverse the eutrophic status of the lake. Probably, the two most obvious indicators of Lake Erie eutrophication are the anaerobic hypolimnium in the Central Basin and excessive algal growth. The management plan should reduce the area of anaerobic hypolimnium and diminish the peak concentrations of algae in the lake.

Many researchers have concluded that the majority of Lake Erie's problems can be attributed to excessive nutrient inputs to the lake. These nutrients stimulate the phytoplankton (algae) growth which yields excess growth. The excess algae settle and decompose in the hypolimnium. The decomposition process consumes oxygen which is responsible for the anaerobic hypolimnium. The anaerobic hypolimnium reduces the concentration of desirable fish species in the Central Basin. Since the onset of Lake Erie's eutrophication problems, commercial fishing has declined markedly. Further undesirable consequences of excessive nutrients are taste and odor problems in drinking water for lakeshore communities and polluted beaches unfit for recreation.

The excessive nutrients entering Lake Erie include the macronutrients of carbon, nitrogen, and phosphorus and the micronutrients of iron, copper, etc. Mathematical models indicate that of these nutrients, phosphorus is considered to be the limiting nutrient affecting algae growth. Experiments have shown that phosphorous additions to Lake Erie will stimulate algae growth and orthophosphorus concentrations decrease to nearly zero during summer algal blooms. Further, phosphorus is the only macronutrient which is not a constituent of the atmosphere. Thus, it is concluded that since phosphorus is the nutrient which limits the growth of algae in Lake Erie, reducing the input of phosphorus to the lake would be the best procedure for reducing excessive algae growth and consequently reversing lake eutrophication.

In order to reduce the phosphorus influx to Lake Erie it is necessary to determine the sources of phosphorus and the methods by which it is transported to the lake. Basically, there are five sources of phosphorus into the lake; atmospheric fallout shoreline erosion, direct point sources, river basin sources, and bottom sediments. No attention is given to atmospheric inputs because these are small and uncontrollable. The shoreline erosion inputs of phosphorus are ignored because the phosphorus contained

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in these materials is considered unavailable for algal growth. Inputs from bottom sediments will essentially cease if the hypolimnium of the Central Basin does not become anaerobic. Thus, the two important sources of phosphorus are the point sources along the lake shoreline and inputs from river basins.

Experimental data are required for the calculational techniques developed herein. These calculations permit quantative understandings of the sources of phosphorus and an understanding of the processes involved in the transport of this phosphorus to the lake. The experimental data for the shoreline point sources includes the records of various treatment plants along Lake Erie and the Detroit River. The experimental data for the river basins are composed of the measured river flow and the ortho and total phosphorus concentrations at the river mouths' confluence with Lake Erie. Additional experimental data were taken downstream from a point source which was located in the Sandusky River, a Lake Erie tributary. This point source, located at Bucyrus, Ohio, was investigated to distinguish between the point source inputs to river basins and those emanating from fields, forests, and other nonpoint sources.

Different computational methodologies were developed using the experimental data. The first section of this report presents the basic concepts, mass balances, and force relationships used in the proceeding sections of the report. There are two basic mass balances; that applied to the water and that applied to the phosphorus. These mass balances are time dependent since much of the transport occurs during storm water flows in the river basins. Further, the force relationship is considered in the form of flow versus stream cross sectional area dependency. With these basic concepts established, the remaining sections of the report can be understood.

The second section of this report concerns the quantification of total phosphorus input to Lake Erie from river basins and shoreline sources. A computational method called the Flow Interval Method was devised to permit the calculation of total phosphorus influx without measuring the total phosphorus concentration for the entire year. The data requirements for this method are discussed, and it is concluded that a good estimate could be achieved if high flow storms were included in the data. The methodology was extended further to river basins with few total phosphorus measurements. This extension was called the Regional Total Phosphorus Model. It was shown to apply to all river basins with substantial total phosphorus measurements and it was presumed to apply to other basins. The study conclusions indicate that basin inputs were significant and would have to be reduced if eutrophication was to be lessened.

Another important aspect of reducing total phosphorus influx from river basins is the understanding of the transport processes in rivers. The third section of this report concerns the transport of total phosphorus during storm events. Basically, the unsteady water mass balance indicates that the water velocity should be slower than the storm wave velocity.

However, it was noted that the total phosphorus peak always preceeded the water peak. The computations in the third section demonstrate that the only

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feasible explanation of this phenomena is for there to be a resuspension and deposition of the total phosphorus from the banks and bottoms of the streams during storm events.

The fourth section of this report presents the derivation of the necessary equations used to calculate the distance of the travel density function from measurements of the water flow rate and the total phosphorus concentrations at a point in the stream. From this information, the average travel distance for total phosphorus can be calculated and the fraction of material carried a given distance can also be obtained. In general, it was found that for large storms the total phosphorus was transported greater distances than small storms. It was also found that the travel distance was shorter in the upstream tributaries than in the downstream mainstem stations. It must be emphasized that these calculations only apply at the point of measurement.

The above calculations indicate that a considerable portion of the total phosphorus in transport during a storm event never reaches the lake. Thus, the question has been raised as to the fate of point source phosphorus entering the river at some upstream point. A calculational technique used to analyze upstream point source inputs is presented in Section Five of this report. This analysis applies during steady flow in contrast to all the other analysis which were performed on storm events. The computational technique uses the method of moments to determine the rate of disappearance of orthophosphorus from the water column, presumably into the sediments during steady flow. A least squares method for fitting the diurnal peak of orthophosphorus concentrations coming from the treatment plant was devised. This analysis indicated that the orthophosphorus coming from the treatment plant at Bucyrus, Ohio, did not discharge directly into Lake Erie but rather it was deposited into the sediments of the Sandusky River. Presumably, the next storm event which passed through the river basin resuspended this phosphorus as total phosphorus and carried it toward the lake. This analysis illustrates that the point source phosphorus in the upstream reaches of the river basin apparently has significantly less impact on Lake Erie than the point sources along the shoreline.

This introduction shows the importance of phosphorus in relation to the restoration of Lake Erie. The various computational techniques presented herein aid in the understanding of total phosphorus transport from river basins in Lake Erie. This understanding will be used in the development of management strategies for the restoration of Lake Erie.

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EQUATIONS

The basic hydrodynamic principles as used for the calculational procedures in the following sections will be reviewed. In particular, the conservation of mass for both the water and the nutrient of interest will be given. Also, a discussion of the slow versus cross sectional relationship, as it applies to the solution of the mass balance equations, will be presented.

Eulerian Point of View

The usual mass balance on water flowing in a stream is formed on an incremental distance and change in time and is the Eulerian point of view. The derivation can be found in many texts (1) and the resulting equation expressing this conservation of water mass is given below:

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = q \qquad (1)$$

where A = water cross sectional slow area at x & t
Q = volumetric flow rate at x & t
x = distance downstream
t = time
q = net volumetric water inflow per unit river length at x & t

This equation contains two dependent variables Q and A, and two independent variables x and t. Since there are two dependent variables and only one equation, this equation cannot be solved by itself. The additional relationship will be discussed later. Also, the net inflow must be specified as a function of time and distance; thus, net inflow includes such phenomena as tributary or sheet flow inputs and ground water inflow or efflux.

In addition to the mass balance on the water, a mass balance on the nutrient of interest, mainly total phosphorus, must be made. Following the same procedure as used for the water, the equation describing the conservation of mass for total phosphorus can be derived and is given below:

$$\frac{\partial AC}{\partial t} + \frac{\partial QC}{\partial x} = qC_1 \qquad (2)$$

where C = concentration of substance at x and t
C_1 = inflow concentration q substance at x and t

Performing the differentiation of the products gives the following:

$$A\frac{\partial C}{\partial t} + C\frac{\partial A}{\partial t} + Q\frac{\partial C}{\partial x} + C\frac{\partial Q}{\partial x} = qC_1 \qquad (3)$$

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Substituting the mass balance on the water (Eq. 1) in Equation (3) yields the following simpler equation which was used on all the Eulerian analysis:

$$A \frac{\partial C}{\partial t} + Q \frac{\partial C}{\partial x} + C \left(\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} \right) = q C_1$$

$$A \frac{\partial C}{\partial t} + Q \frac{\partial C}{\partial x} = q (C_1 - C) \tag{4}$$

This equation gives an additional relationship, but it also adds another dependent variable, C. Now there are two equations (1 and 4) to solve for three variables Q, A, and C. To complete these differential equations, it is presumed that q and C_1 are known as functions of distance and time and that the initial and boundary conditions are known for each of the two equations. Also, it should be noted that the dispersion term is neglected from Equation 2 and hence Equation 4. This was done for two reasons; first, most of the time these equations are used for unsteady flow for which there are few values for dispersion coefficients, and second, the equations are solved numerically which introduces some dispersion into the solution.

Even if the initial conditions, the boundary conditions, and the inflow functions, q and C_1 are known, it is still not possible to solve these equations without another relationship. Normally, this is provided by a force (or as it is sometimes called momentum) balance. In many instances this force balance is dominated by the friction term; in such instances there exists a unique relationship between the river volumetric flow and the cross sectional area. Thus, instead of using an empirical relationship such as the Chezy equation, the measured relationship of Q vs A as obtained from the river point of interest is used. This relationship is shown in Figure 1.

Mathematically, Figure 1 can be expressed as

$$A = f(Q) \quad \text{or} \quad Q = f(A) \tag{5}$$

Now, it is possible to solve Equations 1, 4, and 5 with known initial conditions, boundary conditions, and input functions. When the transport of nutrients is considered from the Eulerian point of view, these are the equations used. The assumptions involved in deriving equations must be remembered when results derived from them are interpreted. In particular, the assumption of no dispersion, the assumption of a unique flow vs. area relationship should be checked.

Lagrangian Point of View

In addition to the Eulerian point of view, the following sections sometimes utilize the Lagrangian point of view, i.e., the observer moves with the flowing water instead of being fixed in space. For Langrangian considerations, we are interested in the location of a water parcel, S, as a function of time and this relationship is given below.

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$$\frac{ds}{dt} = v_w \tag{6}$$

where S = position of water relative to fixed surroundings
v_w = water velocity

The water velocity is obtained as the chord of the Q vs. A curve as shown in Figure 1.

In addition to the relationship of the water parcel position to the fixed surroundings (which have a velocity of zero), interest is focused on the position of the water parcel relative to the water wave (hydrograph) in the stream. This position is described by the following relationship.

$$\frac{dz}{dt} = v_w - v \tag{7}$$

where Z = position of water parcel relative to water
wave in river
v = wave velocity

The wave velocity is determined as the tangent to the Q vs. A curve as shown in Figure 1.

Summary

The basic equations to be used in the following sections are the conservation of mass for both the water and the nutrient and the Q vs. A curve in its measured form. These equations are derived for both the Eulerian and Lagrangian point of view. Their solution requires a knowledge of boundary conditions, initial conditions, and/or input flows and concentrations. Sometimes these equations are turned around to calculate the input functions, sometimes they are linearized, but always the principles of conservation of a mass is applied.

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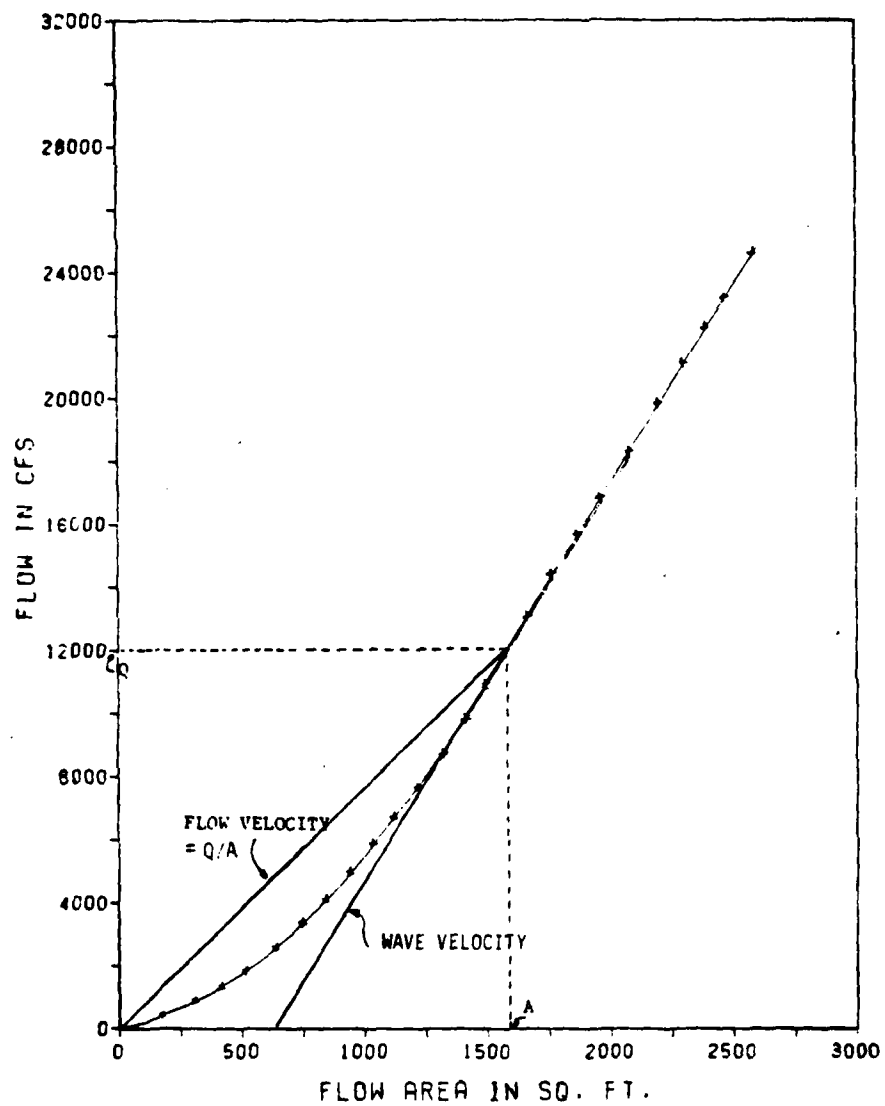
Figure 1. Discharge vs. Flow Cross-sectional Area

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THE ESTIMATION OF NUTRIENT TRANSPORT IN RIVERS

by

F. H. Verhoff

Department of Chemical Engineering
West Virginia University
Morgantown, West Virginia 26505

and

S. M. Yaksich
and
D. A. Melfi

Lake Erie Wastewater Management Study
U. S. Army Corps of Engineers
Buffalo, New York 14207

Acknowledgment

Introduction

The eutrophication of many lakes and the decline of water quality in rivers has been attributed to the increase in phosphorus concentration in these waters by human activity. Abatement schemes to reduce phosphorus inputs have been implemented to alleviate the water quality problems in these lakes and streams. However, the quantitative effect of these point source phosphorus removal projects on the downstream receiving rivers and lakes is not known because the dynamics of phosphorus transport in rivers is not understood. The efficacy of the abatement is determined by improvement in the quality of the receiving water after the treatment implementation. One quantitative and faster measure of phosphorus abatement would be the reduction of phosphorus transport by the river into which the abated point sourced emptied.

Further, there have been many mathematical models of rivers and lakes which purport to predict future water quality. Most of these models are for lakes or downstream segments of rivers and they use the nutrient loadings of tributaries and upstream river segments as inputs to the models. These loadings are often estimated based upon factors which are supposedly correlated with the population or land area of the given river basin. The literature clearly indicates that these correlation factors vary by as much as a factor of five and hence the models are only good to this accuracy.

In order to better understand and hence manage our water resources, it is imperative that the nutrient dynamics in rivers be understood. This paper addresses the problem of posphorus dynamics, presents a calculated technique by which the phosphorus loadings can be estimated from experimental data, and applies the procedure to tributaries of Lake Erie. In addition, this technique is extended to the estimation of phosphorus loadings in rivers with minimal measurements of total phosphorus concentration.

Previous Investigations

The general problem of phosphorus flux determination for a given river basin would appear to involve land use, rainfall, temperature, and other parameters intrinsic to the basin. Various facets of the relationship of phosphorus concentration and flux to these parameters have been investigated in the past. Generally, one can say that of all the factors influencing phosphorus flux, the flow rate of the river dominates.

Wang and Evans (13) determined the concentration of various nutrients including soluble orthophosphate at a one meter depth in nine different stations in the Illinois River during 1967. They found an inverse relationship between orthophosphate concentration and flow; this relationship is commonly referred to as the dilution effect. Enviro Control (3) examined the time and flow records of 142 sampling stations on different rivers throughout the United States and found that orthophosphate predominately exhibited the dilutional effect. However, total phosphorus concentration generally increased with increasing flow rate. Since orthophosphate was a small percentage of the total phosphorus, the major portion of phosphorus transport in river occurs during high flow rate periods, i.e., during storms. Kemp (6) attributed the increasing phosphorus concentration to scouring of bottom sediments

during increased flow. He also states that a significant amount of phosphate accumulation occurs in the sediments during low flows as caused by the absorption on clay materials and by assimilation by periphyton. Other investigators have found correlations between flow and other nutrient concentrations (Johnson (5) and Fuhs (4)).

The fact that total phosphorus concentration depends upon river flow rate has not been used in the calculation of total yearly phosphorus flux for rivers. One procedure often used is based on the loading factor as a function of the population in the upstream river basin or the land area above the point of loading estimation in the river. To illustrate the variability in these factors, the literature values of loading per unit area are shown in Table 1. It can be seen that these factors can vary by several orders of magnitude. Thus, by judiciously choosing these factors based on area or population or a combination of both, it is possible to calculate different levels of phosphorus fluxes and to reach variant conclusions for the same river. For example, by choosing high population factors and low agricultural factors it can be concluded that most of the total phosphorus is of municipal origin. The variability of these factors for the rivers considered in this study will be emphasized later.

Further procedures for the calculation of the river flux involves use of actual total phosphorus concentrations and river flows taken at the river point of interest. The first calculational procedure uses the product of the average flow times the average concentration to estimate the total phosphorus flux. The second procedure essentially calculates the average of the product of the flow and the concentration. In the third procedure, the flux is calculated from the flow weighted average concentration times the total flow for the given river for the time period of interest. Baker and Kramer (1) discuss these procedures and conclude that considerable variability exists in these techniques. This variability results from the dependency of total phosphorus concentration upon river flow rate. In the Lake Erie Report (8), it was concluded that to properly estimate total phosphorus fluxes, high flow events must be sampled and that as many as 48 total phosphorus measurements a year in a given stream could be insufficient to yield a good estimate of the flux if high flow events were missed.

The general conclusion resulting from the survey of the literature suggests that the present techniques for phosphorus load estimation are deficient. Hence, a better loading calculation method is needed which also yields an estimate of the error associated with the flux estimate.

Goal of the Present Work

Since certain facts are known about the dynamics of phosphorus transport in rivers and since phosphorus fluxes in rivers are important data for evaluation of phosphorus abatement programs and prediction of eutrophication potential of water bodies, it would seem logical to try to utilize known river properties in the estimation of loadings. This paper contains a description of the methodology developed and used for the estimation of the total phosphorus loading into Lake Erie. To make these estimates, there are two fundamental but related problems to be attacked. First, since it was

Table 1 - Phosphorus Flux Estimates Based
Upon Population or Land Area

Investigation	Range of Loading Factors
Population Estimates	
U.S.E.P.A. Working Paper #22 Eutrophication Survey (9)	0.36 to 1.72 kg Total Phosphorus per Person per Year
U.S. Army Corps of Engineers Lake Erie Study (8)	0.08 to 1.94 kg Total Phosphorus per Person per Year
Area Estimates	
U.S.E.P.A. Working Paper #25 Eutrophication Survey (10)	3 to 128 kg Total Phosphorus per Square Kilometer per Yr.
Uttormark et al (11)	11 to 5300 kg per Square Kilometer per Year

( ) Refers to Reference Number

impossible to sample and analyze a river at time intervals frequent enough to accurately integrate the product of the concentration and the flow over the course of a year, some procedure for the estimation of the total yearly flux of phosphorus from a limited number of samples must be devised. Secondly, it was also impossible to institute a sampling program in all the rivers which empty into Lake Erie, and thus there was needed a scheme for the estimation of phosphorus fluxes from river basins in which a minimum of phosphorus concentration data was available.

Herein is presented an estimation scheme for the expected value of the phosphorus flux in a particular river and for the standard error associated with the expected value. The procedure essentially involves the experimental establishment of a relationship (either a curve or a group of data) between the flow rate and the phosphorus flux (flow times concentration). This curve is then employed in conjunction with flow data for the entire year to estimate the flux and the standard error. Thus, this procedure required a limited sampling program for the establishment of the flux flow curve.

For the rivers in which no phosphorus measurements were made, a similar procedure was used except that the curve relating phosphorus flux to river flow rate had to be generalized such that it would apply to all rivers of the Lake Erie basin. The only experimental data required for the rivers with little phosphorus information was the daily flow data, the base phosphorus concentration from the historical record, and the area of the watershed. All of this information was readily available for all the important streams flowing into Lake Erie.

Phosphorus Dynamics in Rivers

The procedure for phosphorus flux estimation developed in this report is based upon a knowledge of the dynamics of phosphorus in river basins. From previous research studies, it has been documented that phosphorus concentrations generally increase with increasing flow. Cahill (2) reported that for the Brandywine River the phosphorus concentration definitely peaks before the water flow rate reaches its maximum. Some data taken on the Sandusky River as an integral part of this study also indicates this same characteristic. This data is shown in Figure 1. If one is to use this phenomena in phosphorus flux estimation, then the correlation should take into account the time as well as the flow rate of the river. The relationship between flux and the two variables, river flow, and time into the storm were investigated.

In the development of a correlation, the flow rate of the river can be quantified from the stage reading. In our calculations we will be using instantaneous flow for the correlations and daily average in the flux calculations. There may be some error introduced by this procedure, however, it should be minor compared with other errors because of the large river basin studied. The ideal situation would be to have both data in terms of instantaneous flow rate, but that data is not historically available. Walling (12) has shown that the use of daily average flow measured to estimate sediment flux can lead to large errors on small rivers.
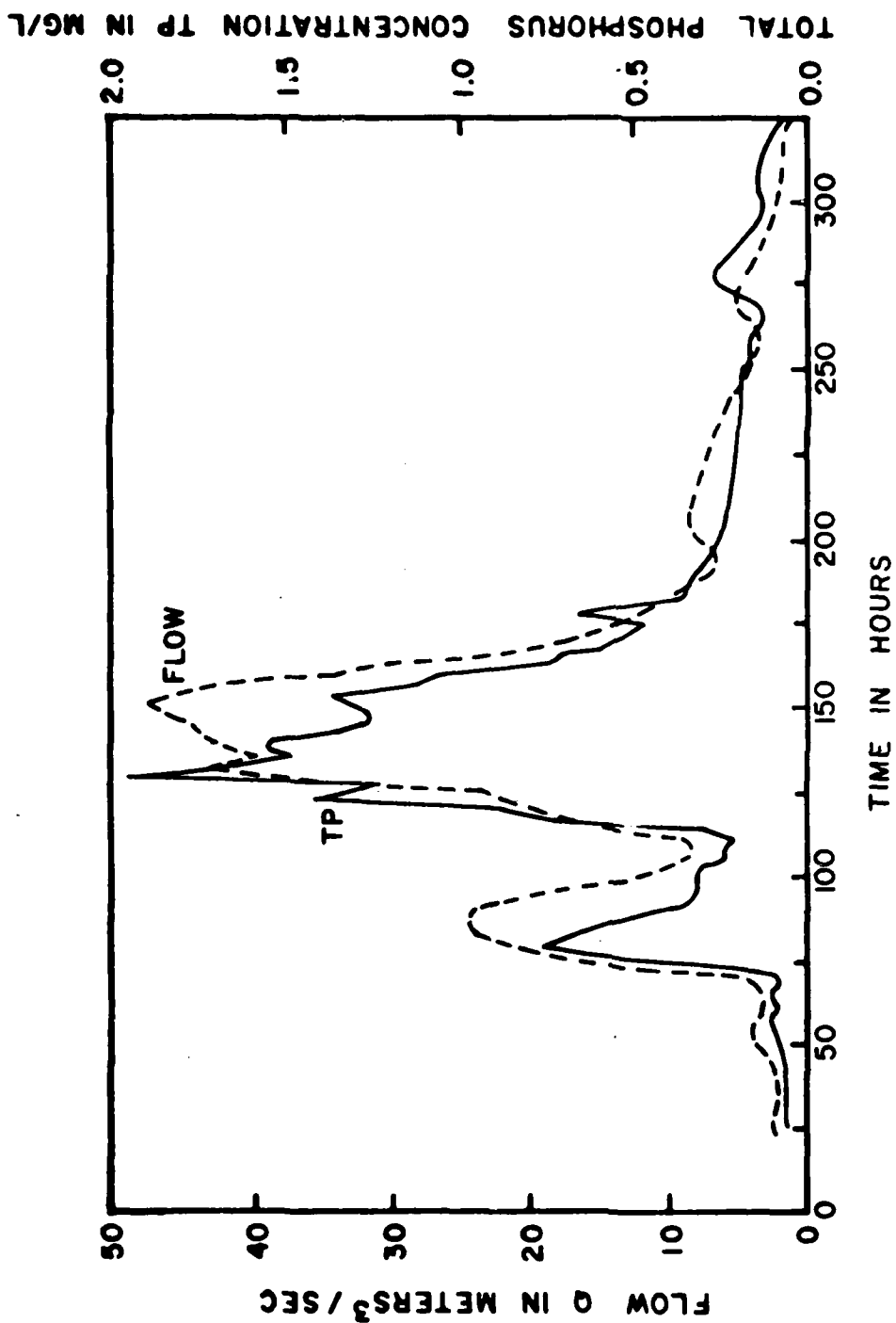
Figure 1. Total phosphorus concentration and water flow as a function of time on the Sandusky River.

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The second parameter of correlation, the time since the beginning of storm, is not nearly as easy to quantify as the river flow rate. Two different parameters were used; the first is the day of the storm and the second is the total water flow of the four previous days. The day of the storm is a direct measure of time into the storm but it is not easy to use because it is sometimes difficult to determine which day the storm began. Further, this procedure only measures the time to within one day accuracy and as can be seen from the hydrograph of Figure 1 the storm phenomena time scale is certainly less than one day. This correlation was attempted for data taken in the Sandusky River basin, and shown in Figure 2. In this figure, the phosphorus technique for each of the first three days of the storm is shown. It can be seen that the steepest slope for this correlation line occurs for the first day of the storm. The second and third days have successively lower slopes.

It would be expected that the average of the four previous daily average flow rates to give some indication of the time past since the beginning of the storm. If the average of the four previous flow rates are lower than the flow on a given day, then that day is the initial part of a storm. On the other hand, if the average of four previous days is larger than the flow on the given day, then the river would be in the declining stage of the storm. Again, a least squares technique was employed to correlate the phosphorus concentration with, in this case, the two parameters, the instantaneous flow rate and the average of the flow rate for the previous four days. One relationship which would be used is an equation of the following form:

$$C_{TP} = 0.148 - 5.9 \times 10^{-5} F_A + 3.1 \times 10^{-4} Q$$

where $\quad C_{TP}$ = Total Phosphorus Concentration
$\quad\quad\quad F_A$ = Flow Average for the Four Previous Days
$\quad\quad\quad Q$ = Instantaneous Flow Rate

This equation contains the least squares coefficients as determined for storm data taken at a station on the Sandusky River. This form of least squares always yields the same slope of the curve of phosphorus concentration versus flow rate with the intercept being a function of the average flow of the four previous days. To permit a variation of both slope and intercept, the following form of equation was used in the least squares.

$$C_{TP} = a_1 + a_2 F_A + a_3 Q - a_4 Q F_A$$

where a_i are arbitrary constants

The coefficients of the equation were obtained for data from the Sandusky River and this data and the least squares lines are plotted in Figure 3. As can be seen from the figure, a low value of the average for four previous days yields a larger slope on the graph as would be expected.

These investigations indicate that both the river flow rate and the time since the beginning of the storm have significant effects on the concentration of phosphorus in the river. However, the time of the storm is somewhat difficult to quantify and hence it was decided not to include this variable in the present estimation techniques. Not including this variable
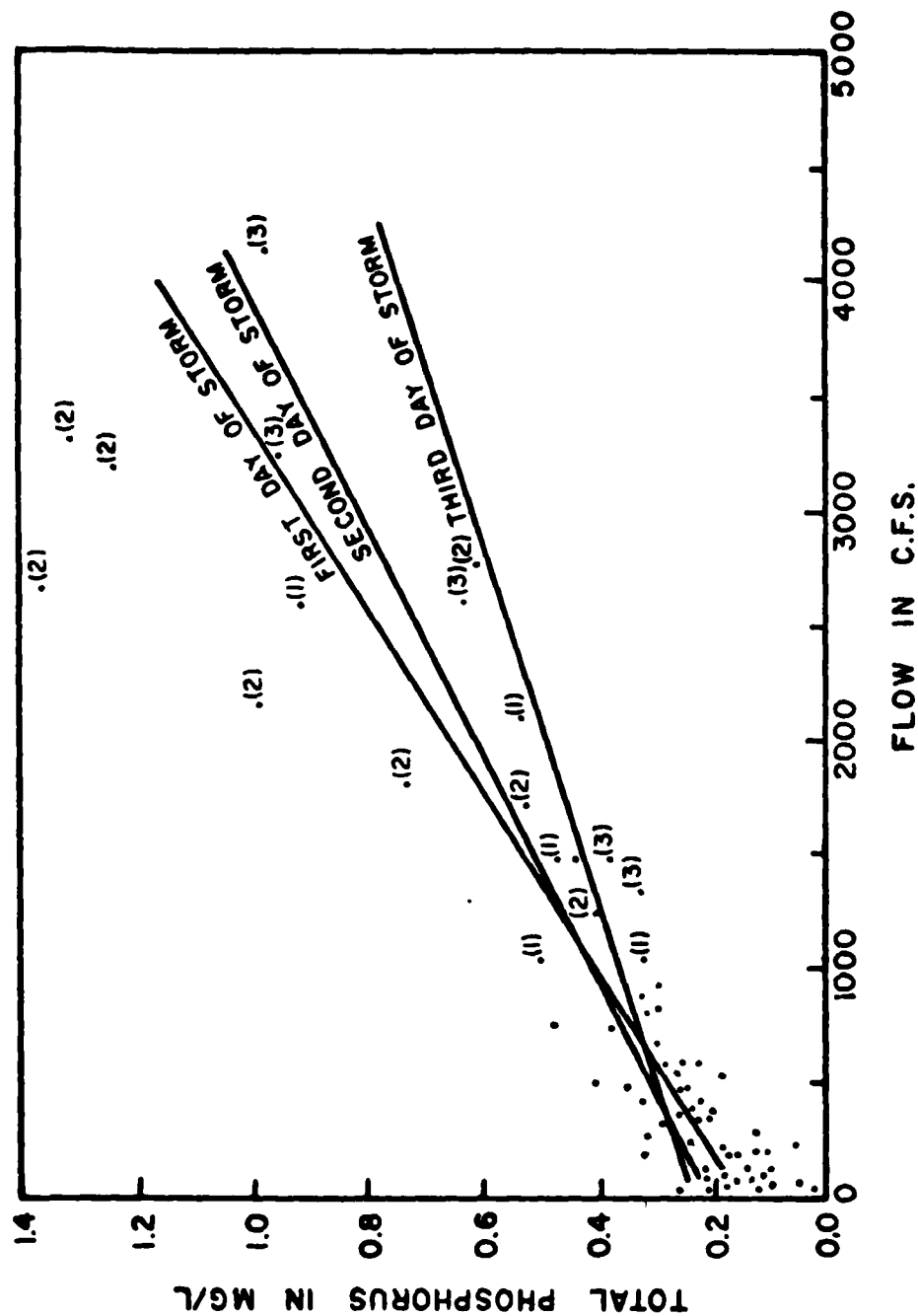
Figure 2. Total phosphorus concentration vs. river flow rate with day of storm as a parameter. The least squares correlations for each day of the storm is indicated. The number in parenthesis indicates the day of storm.

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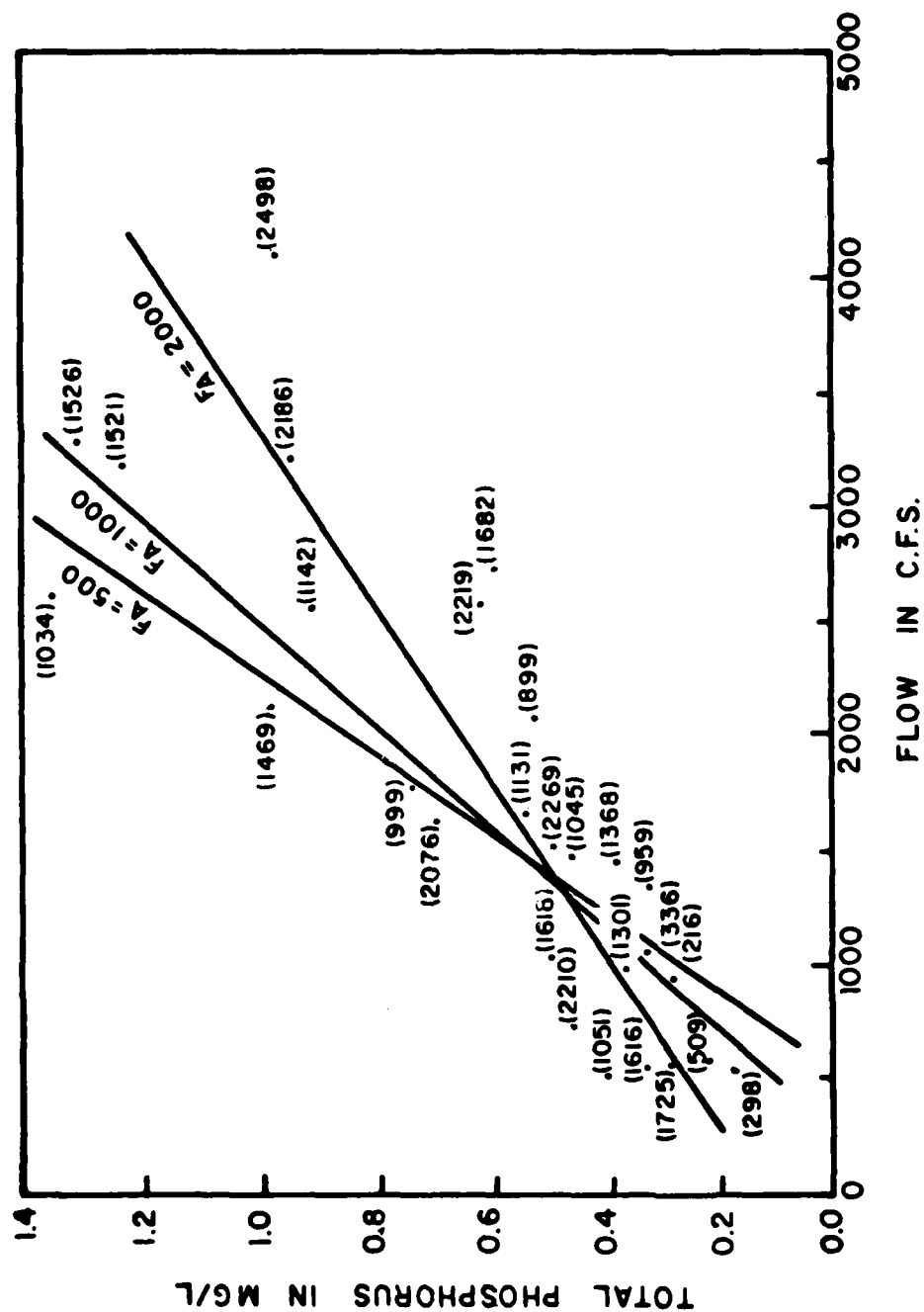
Figure 3. Total phosphorus concentration as a function of river flow rate and the average flow rate of the prior four days. The lines represent least squares fits to the data. F_A is the four previous days average flow and is indicated in parenthesis.

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does not necessarily imply that the phosphorus fluxes calculated will be less accurate, rather it implies that the variance associated with the estimation technique (for a given number of experimental measurements) will be larger. Hence, the equivalent accuracy can be achieved by ignoring the time into the storm, if more experimental data points are used in the correlation of flow versus concentration, that would be used in concentration versus flow and flow average of the previous four days. For this estimation of phosphorus flux into Lake Erie, the only parameter considered important will be the flow rate.

Estimation Procedure for Measured Basins

The flux estimation procedure for each river basin in which concentration and flow measurements have been made is based upon a technique called the flow interval method. Baker and Kramer (1) and Porterfield (7) used the basic idea of the interval method previously. This method essentially involves the plotting of the product of the total phosphorus concentration times the flow rate (i.e., the total phosphorus flux) as a function of the river flow rate. This dependency of flux with river flow rate is then used with the daily average river flow records to calculate the yearly total phosphorus flux.

An example of the data used in the phosphorus flux estimation is shown in Figure 4. This river data illustrates the quadratic character of the data when plotted as total phosphorus flux as a function of river flow rate. If the total phosphorus concentration were plotted versus river flow, a linear relationship would result. This graph of total phosphorus flux versus river flow rate is then used in the estimation technique by dividing the maximum flow rate (Q_m) into n equal segments. The length of each segment is then

$$Q = Q_m/n$$

If $Q_i = i \times Q$, then the "i" flow interval contains all river flows greater than Q_{i-1} and less than Q_i. In each of the "i" intervals there are k_i data points whose flux values are given by L_{ij}. The average flux value for each interval is then calculated by the following formula.

$$\bar{L}_i = \sum_{j=1}^{ki} L_{ij}$$

The standard error of the mean then can be calculated for each interval based upon the following formula.

$$\bar{S}_i^2 = \frac{\sum_{j=1}^{ki} (L_{ij} - \bar{L}_i)^2}{k_i (k_i - 1)}$$

Although it is known that $\bar{L}_i$ is distributed normally and that $\bar{S}_i$ is chi-squared and that any confidence interval for the "i" flow interval should involve the students t distribution, other known and unaccounted errors in the system mitigate against expending the extra effort to carry the exact statistics through the problem. Thus, for these calculations it will be

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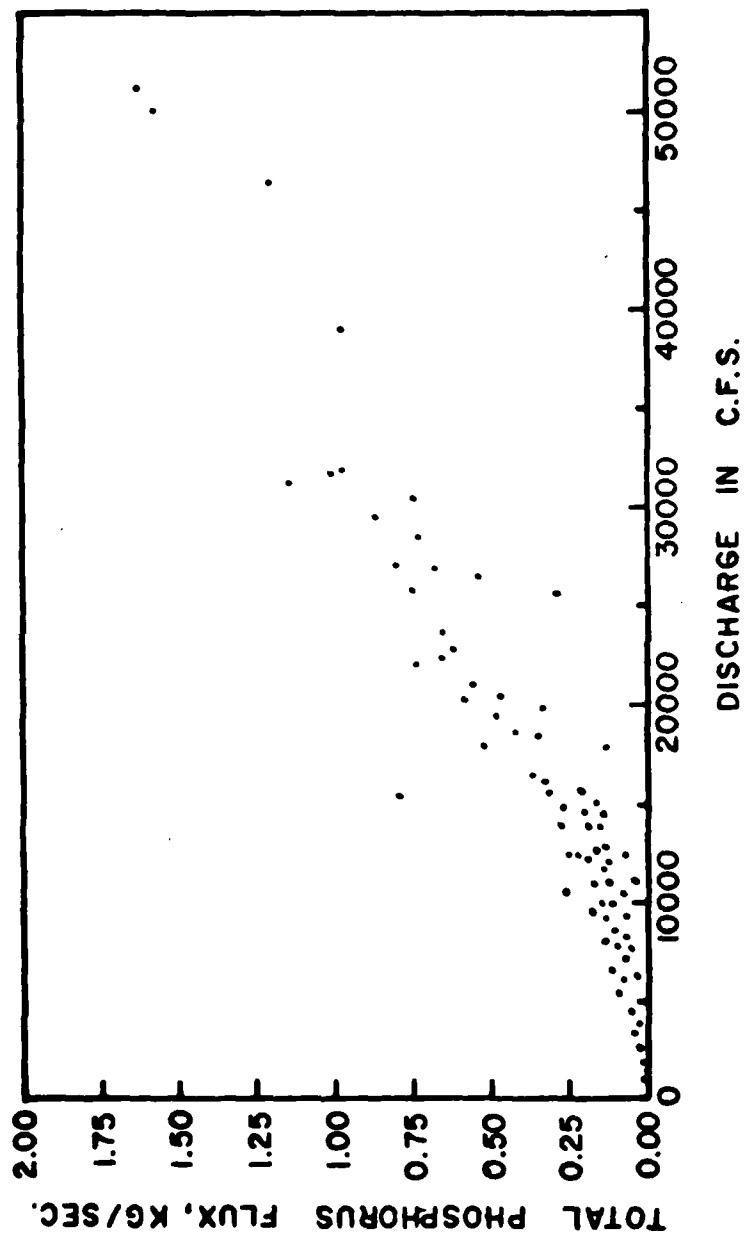
Figure 4. Total phosphorus flux as a function of river flow rate for the Maumee River during spring 1975.

presumed that the average for each interval is distributed normally with mean L_i and variance $\bar{S}_i$.

In order to compute the total phosphorus flux for a year or any other period of time, it is necessary to determine the number of days during the time period that the flow was in each flow interval on the graph. The probability, P_i, that the flow occurs in the "i" interval, is given by the following formula.

$$P_i = \frac{d_i}{D}$$

where P_i = The probability that flow occurs in the "i" interval during a given period of time.

d_i = The number of days in the given time interval in which the flow rate was in the "i" interval.

D = The total number of days in the given time period.

The average daily flux of total phosphorus for the given time period is then calculated from the following formula:

$$\bar{L} = \sum_{i=1}^{n} L_i \, P_i$$

An approximation for the variance associated with this estimated average daily flux is calculated by the equation below.

$$V = \sum_{i=1}^{n} \bar{S}_i^2 \, P_i^2$$

Since it was presumed that the average total phosphorus flux for each flow interval was distributed normally, the weighted sum of this random variable will again be distributed normally. Thus, the confidence interval for the average daily total phosphorus flux will be given by the following formula.

$$L = \bar{L} \pm k_r \sqrt{V}$$

Where k_r is the factor for r percent confidence interval based upon the normal distribution with mean zero and variance one.

It must be remembered that the assumption of the normal distribution instead of the students t distribution in each of the flow intervals will tend to reduce the estimated confidence interval. However, for a reasonably large number of measurements, the estimates based upon the normal distribution approaches these from the students t distribution.

In order to calculate the total flux of total phosphorus for the given period of time, the average daily total phosphorus flux is multiplied by the number

of days in the time period. Similarly the confidence interval is calculated
by multiplying the daily variability by the number of days.

Application to the Maumee and Sandusky Rivers

In this section, the flow interval method of total flux estimation will be
compared with three other estimation schemes. Also, the amount and type of
concentration data which are required to obtain good flux estimates will be
discussed. For water years 1956 on the Sandusky River and 1957 on the Maumee
River, 48 measurements (four per month) of suspended sediment concentration
and water flow rate were randomly selected from daily concentration and flow
data. Four different methods for the estimation of the total phosporus flux
were used. (Table 2). Method A was the multiplication of the average flow
times the average concentration for the 48 measurements. Method B simply
involves the calculation of the flux for each day and then averaging these
fluxes. Method C obtains an estimate of the average daily flux by
multiplying the flow weighted average concentration times the average daily
flow. Method D is the flow interval method presented in the previous sec-
tion. No comparisons will be made for Method A since it will obviously
underestimate the suspended sediment flux since the concentration increases
with increasing flow.

Comparison of the suspended sediment loads for the Maumee River show that
each of the three methods calculate an average flux which is less than the
actual flux of 3,300 tons/day based on 365 measurements. However, the error
estimate for the flow interval method is 40 percent versus 63 percent for
each of the other methods. The reason for the low flux estimate is that not
enough high flows were included in the sample of 48.

Comparion of the flux data for the Sandusky River for water year 1956 shows
that the flow interval method yields a better estimate and smaller error than
Methods (B) or (C). The Sandusky estimate using the flow interval method is
better than the Maumee estimate using the same method because the day which
carried the highest sediment load was included in the Sandusky sample.

Table 3 illustrates the ability of the flow interval method for estimating
the entire year average flux from limited concentration information with a
well defined flux versus flow curve. For the Maumee River, 48 samples
selected uniformly were compared with 48 samples selected during the four
major flow events. It can be seen from the table that the selection of the
event information yielded a better estimate (3,453 + 464 tons/day) and
smaller error (13 percent) than the four times monthly strategy (2,283 + 922
tons/day) and (40 percent error) when compared to the actual load, (3,300
tons/day).

When only three flow events (36 samples) were included with the high flow
event omitted, a poorer estimate (2,136 + 412 tons/day) was obtained, even
though the error estimate was small. When three flow events which included
the high flow were selected (36 measurements) a good flux estimate (3,486 +
467 tons/day, 13 percent error) was obtained. Including only the two high
flow events (24 measurements) again yielded good flux (3,789 + 502 tons/day)
and error estimate (13 percent). Using only the high flow event

Table 2 - Comparison of Load Calculation Methods (Tons/Day)

	Maumee River Water Year 1957	Sandusky River Water Year 1956
Actual Load (365)	3,300	911
Method (B) Load, avg. daily (48)	$2,324 \pm 1,464$ $\pm 63\%$	$1,757 \pm 1,687$ $\pm 96\%$
Method (C) Load, wt mean (48) x mean flow (365)	$2,352 \pm 1,481$ $\pm 63\%$	$1,522 \pm 1,461$ $\pm 96\%$
Method (D) Load, avg. daily flow, interval (48)	$2,283 \pm 922$ $\pm 40\%$	$1,140 \pm 696$ $\pm 61\%$

( ) Number of measurements included in sample.

Table 3 - Comparison of Sampling Strategies with Flow Interval Method (Tons/Day)

	Maumee	Sandusky
Actual Load (365)	3,300	911
Four Times Monthly (48)	2,283 $\pm$ 922 $\pm$ 40%	1,140 $\pm$ 696 $\pm$ 61%
Four Flow Events (48)	3,453 $\pm$ 464 $\pm$ 13%	
Three Flow Events Missing High Flow Event (36)	2,136 $\pm$ 412 $\pm$ 19%	
Three Flow Events With Highest Flow Event (36)	3,386 $\pm$ 467 $\pm$ 13%	
Two Flow Events With High Flow (24) Maumee (22) Sandusky	3,789 $\pm$ 502 $\pm$ 13%	1,045 $\pm$ 411 $\pm$ 39%
High Flow Event (17)	2,984 $\pm$ 757 $\pm$ 25%	

( ) Number of Measurements

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(17 measurements) also gave a good flux estimate (2,984 ± 757 tons/day), however, the error estimate increased to 25 percent.

Comparison of sampling strategies for the Sandusky River shows that sampling the two high flow events (22 measurements) yields a better flux estimate (1,045 ± 411 tons/day) and error estimate (39 percent), than 48 measurements made four times monthly (1,140 ± 696 tons/day and 61 percent error estimate) when compared to the actual flux (365 measurements) of 911 tons/day.

The reason a better flux estimate and smaller error estimate is obtained for the Maumee River than for the Sandusky River is that a flow event lasts 10 to 14 days on the Maumee. On the Sandusky, a flow event lasts only five to nine days. Therefore, 12 measurements over the hydrograph averages one measurement per day for the Maumee. For the Sandusky, daily measurements are not enough. To obtain good definition for the Sandusky, measurements should be taken at least every 12 hours, or 12 measurements in six days. For a stream which rises and falls in one day, measurements should be taken about every two hours.

In summary then, it is concluded that the flow interval method will yield good estimates of the flux if the high flow portion of the flux versus flow curve is defined.

Regional Phosphorus Load Model

In a previous section, it was shown that the flow interval method yields good estimates of the flux if enough high flow measurement points are included in the data base. Thus, to estimate the phosphorus flux for a given river basin it is only necessary to measure the phosphorus flux as a function of flow rate for several high flow events and then utilize the daily average flow record to calculate the total flux. Hence this procedure could be used for all the basins in which sampling was performed during this study.

However, the sampled river basins only constituted one third of the total drainage area into Lake Erie. To complete a phosphorus flux estimate into the lake, it is necessary to calculate the fluxes from the other two thirds of the land area. In other words, a methodology had to be developed which would permit the computation of the phosphorus fluxes for many river basins which had a very limited chemical sampling history and had the flow record from a stream gaging station.

Since the previous calculations indicated the importance of measuring high flow events in a river basin and since no historical records contain these measurements, it was necessary to attempt an extrapolation from the basins measured during this study into those unmonitored rivers. The extrapolation need only involve the relationship between phosphorus flux and river flow rate, because once this information is known, the flow interval method can be employed using the stream flow data from the gage. The problem then is the determination of the general relationship between phosphorus flux and river flow rate which will apply to all rivers in the Lake Erie basin. Fortunately, the sampling program involved rivers from the far west to the east of the lake encompassing most terrain and soil types. Thus if a general

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relationship for the phosphorus flux as a function of flow rate could be found for these rivers it probably would apply to all the rivers of the Lake Erie basin.

The initial attempts to achieve this general correlation focused on the four monitored rivers of western Lake Erie, i.e., the Maumee, the Portage, the Huron, and the Sandusky Rivers. These rivers had the same range of phosphorus concentration although the flows were quite different because of different land areas. The first task was to find some function of area which would reduce these four rivers to the same flow rate scale. Often the unit area contribution is considered important and this concept would suggest that the flow rate of the river be divided by the area of the river basin. However, the most important time periods of phosphorus flux are the storms. During storms, according to partial area hydrology, only the fraction of the total basin area near the stream contributes to the actual flow observed. For partial area hydrology, the length of the river might be more nearly the characteristic dimension. Since the river length is related somewhat to the square root of the basin area, partial area hydrology then leads to a flow parameter which involves the flow rate divided by the area to a power between one half and one. After plotting the data for the four rivers using different power fractions, it was found that the best fit was approximately the 0.85 power. Figure 3 shows the plot based upon the parameter of flow rate divided by area to the 0.85 power.

Although only a portion of the river basin is contributing to storm flow and phosphorus, the river bottom is contributing phosphorus which is transported during the storms. Hence, on the ordinate in Figure 5, is plotted the total phosphorus flux divided by the total area of the river basin. From this figure it can be seen that all four of these basins are indistinguishable, i.e., this graph could be employed for the prediction of the phosphorus flux of any of these rivers. It appeared that this correlation could be used for all the rivers of western Lake Erie.

If the data from Cattaraugus Creek in eastern Lake Erie is plotted on Figure 5, it is immediately apparent that this data lies significantly below that of the western Erie rivers. Upon further inspection of the data one finds that the total phosphorus concentration of the Cattaraugus is much lower than that found in the Maumee for example. However, the difference between high and low values were about the same. In other words, the Cattaraugus and the Maumee were similar in the increase of total phosphorus concentration with increased flow. They differed in the base value of phosphorus concentration during low flow time periods. This fact suggested that maybe the Cattaraugus and other eastern Erie rivers could be made similar to the western Erie rivers if the base total phosphorus concentration were subtracted from the total phosphorus concentration found during high flow periods and this flux difference plotted against the flow rate parameter.

Figure 6 contains this new flux parameter, the flow times the difference between the total phosphorus concentration and the total phosphorus concentration during base flow divided by the basin area, graphed as a function of the flow parameter. As can be seen from this graph the data from seven rivers (Maumee, Portage, Sandusky, Huron, Chagrin, Vermilion, and
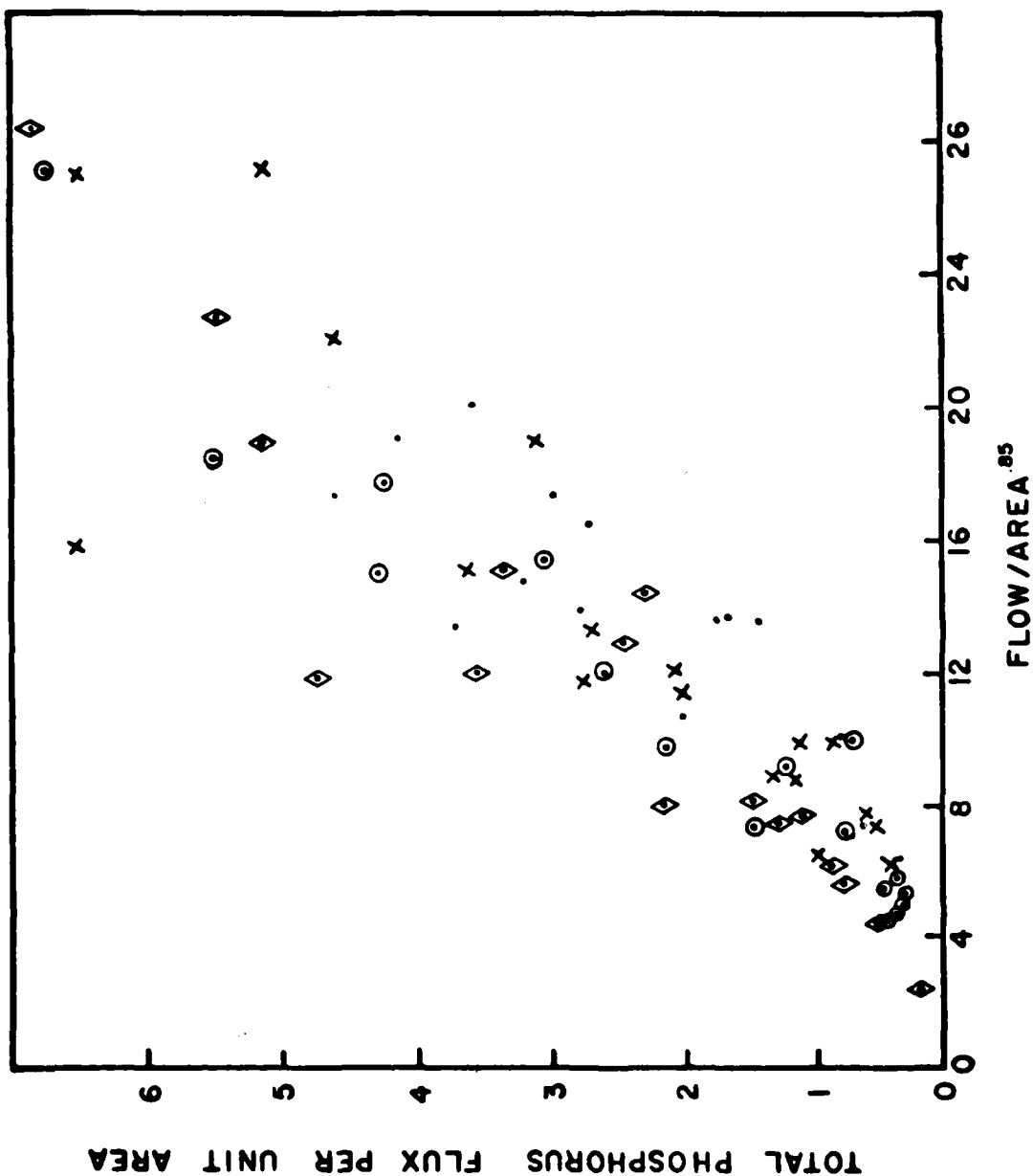
Figure 5. A comparison of the data for four western Lake Erie tributaries when plotted as unit area total phosphorus flux as a function of flow rate divided by area to the 0.85 power. ⊙ indicates the Maumee River, ⬦ indicates the Portage River, • indicates the Sandusky River, and x indicates the Huron River.
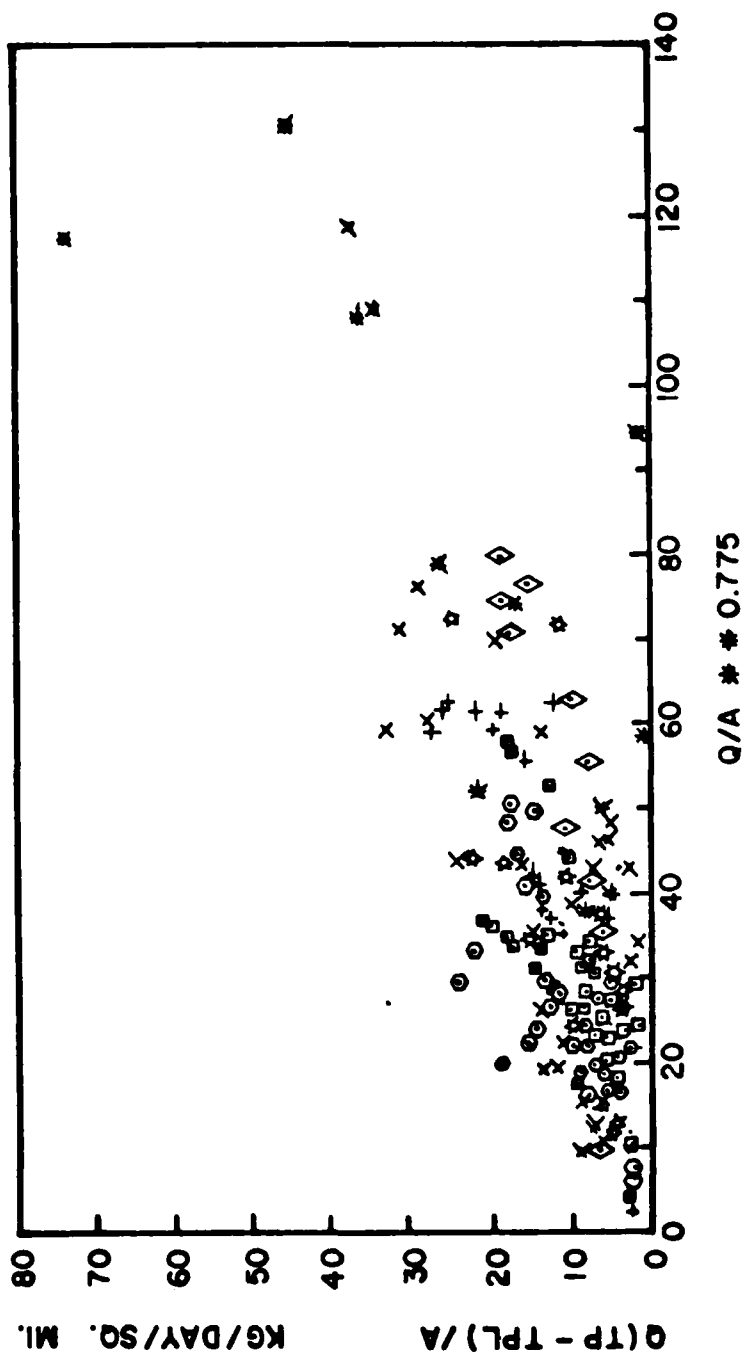
Figure 6. A comparison of seven Lake Erie tributaries on a graph of unit area total phosphorus flux minus base phosphorus flux as a function of flow rate divided by basin area to the 0.775 power. ⊡ is the Maumee River; ⊙, the Portage River; +, the Sandusky River; ×, the Huron River; ◈, the Vermilion River; ✱, the Chagrin River; and ✦, Cattaraugus Creek.

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Cattaraugus), generate the same relationship on this graph. Since these rivers span the length of the lake, it appears that this correlation could be used to estimate the total phosphorus flux for any flow gaged river in the Lake Erie region. Hence the procedure for the calculation of phosphorus loadings based upon this particular correlation will be called the Regional Phosphorus Loading Model.

In Figure 6 the parameter plotted along the abscissa is the river flow rate divided by the basin area to the 0.775 power. This optimal exponent was obtained from the following equation for the curve.

$$\frac{Q\,(P-P_I)}{A} = \alpha \left(\frac{Q}{A^n}\right) + \beta \left(\frac{Q}{A^n}\right)^2$$

or

$$\frac{(P-P_I)}{A^{1-n}} = \alpha + \beta \left(\frac{Q}{A^n}\right)$$

This last equation was fit to 1010 data points with a least squares program. The results are shown in Table 4. The value of n giving the largest multiple correlation coefficient was 0.775 and it was chosen as the optimal value.

Given that the correlation between a parameter related to phosphorus flux and a parameter related to river flow rate has been established, it is possible to calculate the total phosphorus flux for any river for which the flow record is known and for which a base total phosphorus concentration can be obtained from the historical data. In this estimation procedure, the range of daily average flows for a given river is divided into a fixed number of flow intervals. The probability of a daily average flow being in each interval is calculated as in the flow interval method. The average value of the phosphorus flux parameter from the general correlation is calculated for each interval. The standard error of the mean is also calculated for each interval. Using the low phosphorus concentration for the river, the average and the standard error of the mean for the total phosphorus flux parameter are converted into their corresponding values in terms of phosphorus flux for each interval. The flow interval method is then utilized to calculate the average daily total phosphorus flux and the standard error of the mean associated with this value.

There are two salient difficulties with the usage of this technique. First, the general correlation of total phosphorus flux and river flow rate for all rivers as well as the correlations for a specific river involves the instantaneous flow rate. Whereas, the flow rates obtained from published gaging station records are daily average flow rate. Usage of the average daily flow rate should not bias the estimates but only should add to the variance of the estimate. Since the scatter of the correlations is large this additional variability should add little to the standard error of the mean. Secondly, there is sometimes difficulty in determining the base total phosphorus concentration from historical data. Originally the low total phosphorus concentration from historic data was used. However, some data sets tabulate a

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Table 4 - Least Squares Fit Results

n	Coef. of Determination	Variance of Estimate	α	β
0.9	0.2315	0.01575	0.06513	0.00906
0.85	0.2462	0.00800	0.04435	0.00495
0.825	0.2509	0.00574	0.03674	0.00363
0.8	0.2538	0.00414	0.03052	0.00266
0.7755	0.2547	0.00302	0.02554	0.00195
0.775	0.2547	0.00300	0.02545	0.00194
0.75	0.2536	0.00219	0.02131	0.00141
0.7	0.2456	0.00118	0.01516	0.00073
0.5	0.1495	0.00011	0.00484	0.00004

single total phosphorus concentration which is significantly lower than all others measured (zero for example). The question arose as to whether that value was a true measurement or whether it is an experimental error. As a general rule it was best to choose as the low phosphorus concentration the lowest value which occurs two or preferably three times in the historical data set. Close examination of the data revealed that the low total phosphorus concentrations occurred when the flow rate was in the range of 0.5 to 2.0 cubic feet per second divided by area to the 0.775 power. The base phosphorus concentration was then calculated by averaging the concentrations which were measured with flows in this range.

Application of the Phosphorus Load Model to Lake Erie Tributaries

To test the efficacy of the Phosphorus Load Model (PLM) for the prediction of phosphorus loadings for rivers of the Lake Erie basin, internal comparisons were made on the seven rivers whose data comprised the general correlation. Predictions of the total phosphorus loads were computed for all seven rivers using the PLM. Then the data from each river was used separately with the flow interval method to calculate the phosphorus flux of each river. A comparison of the values is shown in Table 5. As can be seen the PLM predicts values which are within the expected errors for all the rivers. The most significant deviation in 1975 occurs in the Cattaraugus, but the intervals overlap and statistically one would expect this type of deviation occassionally. It must be remembered that the deviation interval is 90 percent probable. The conclusion drawn from this table is that the PLM predicts the phosphorus flux almost as accurately as the measured data using the best calculational technique, i.e., the flow interval method. The PLM was thus utilized in all the total phosphorus flux estimates for primarily rural river basins.

The phosphorus load model was applied to most of the tributaries of Lake Erie with the resulting phosphorus transport per unit area listed in Table 6. It can be seen that the unit area loading varies by a factor of three. Further, subtraction of the point source (either reported or on a population basis) does not improve the similarity of the loading factors for these basins. Thus it appears that factors beyond area or population determine the outflow of total phosphorus and that these factors are not easy to discern.

Least Squares Utilization of the Data

Instead of using the actual data points themselves in the flow interval method it is possible to employ the least squares best fit of this data along with the river flow information to estimate the total phosphorus transport. This procedure has been investigated with certain assumptions about the distribution of the random variable contained in the data. The estimation of the daily average flux of total phosphorus is quite straight forward and can be done if so desired from the least squares equation listed in Table 4. The calculation of the variance associated with this estimate is more difficult and requires certain assumptions.

Overall, the use of the least squares does not reduce the effort since the measured river data must be first analyzed on the computer to obtain the

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Table 5 - Comparison of Total Phosphorus Flux for Lake Erie
Tributaries Measured vs. Phosphorus Load Model

River	:	Measured	:	PLM	:	# of Samples
			1974-1975			
			Metric Ton/Yr.			
Maumee	:	2233 + 120	:	2280 + 82	:	262
Portage	:	112 + 5	:	106 + 3	:	281
Sandusky	:	499 + 32	:	532 + 17	:	277
Huron	:	122 + 8	:	138 + 4	:	399
Vermilion	:	75 + 13	:	70 + 3	:	43
Chagrin	:	93 + 17	:	107 + 6	:	41
Cattaraugus	:	146 + 24	:	182 + 12	:	41
			1974			
Sandusky	:	533 + 87	:	679 + 30	:	116
			1972			
Sandusky	:	675 + 75	:	773 + 25	:	30

Table 6 — Unit Area Contributions of Total Phosphorus

	Kilograms Per Hectare Per Year (kg/ha/yr)		
	(a)	(b)	(c)
Maumee	1.36	1.10	.78
Portage	1.01	.036	.37
Sandusky	1.54	1.36	1.19
Huron	1.27	.81	.78
Vermilion	1.11	.88	.79
Black	1.94	1.18	1.34
Rocky	3.01	1.84	-
Cuyahoga	3.29	1.19	-.60
Chagrin	1.46	1.19	-.60
Grand	1.67	1.59	-
Ashtabula	1.56	1.40	-
Conneaut	2.10	1.99	-
Cattaraugus	1.30	1.30	1.02

(a) - Values at gaging stations.
(b) - Value (a) less reported point sources.
(c) - Value (a) less population equivalent point sources.

least squares equation. Since the data is already on the computer, it is expedient to proceed immediately to the flow interval method rather than bother with the fitting equation.

If a quick estimate of the loading of a given river is needed, it is possible to use the least squares fit of the regional phosphorus load model. However, it must be remembered that this model was shown to be useful for tributaries of Lake Erie only. Any extrapolation to other river systems is precarious.

Conclusions

A flow interval method for the estimation of total phosphorus transport rate in rivers is developed. This method requires some measurements of total phosphorus concentration and the daily river flow records. In a comparison with previous methods the flow interval method is shown to be superior.

This method is generalized to all tributaries in the Lake Erie basin. This regional phosphorus load model is shown to be useful for all the nonurban tributaries of the lake. This model was applied to several rivers and the resulting total phosphorus transport was used to calculate the unit area and unit population contributions for these basins. There was considerable variation in the unit contributions among river basins which appeared similar in most respects.

The method as applied in this paper is restricted to total phosphorus. However, it has application to any substance whose concentration is a function of river flow rate. In a previous report, the Corps of Engineers used this technique for calculations of chloride, ammonia, organic and nitrite-nitrate nitrogen, orthophosphorus, silica, and suspended solids transport.

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TOTAL PHOSPHORUS TRANSPORT DURING STORM EVENTS

by

F. H. Verhoff

Department of Chemical Engineering
West Virginia University
Morgantown, WV 26505

and

D. A. Melfi

Lake Erie Wastewater Management Study
U. S. Army Corps of Engineers
Buffalo, New York 14207

Introduction

It is known that the total phosphorus concentration increases with increasing
river flow rate during storm events for many rivers. Cahill et al. (1) found
this to be the case for the Brandywine River in eastern Pennsylvania and the
Corps of Engineers (3) found this same phenomena in the rivers of western
Ohio which drain into Lake Erie. In further work on Lake Erie, the question
arose as to the origin of the total phosphorus passing a given downstream
point in the river during the storm event. Keup (2) suggested that this
total phosphorus comes from the river bottom, banks, and flood plains during
the storm event. Others proposed that the source of this total phosphorus at
a downstream river station is runoff water which comes from some part of the
land area of the basin.

The two views of phosphorus transport which during storms can be summarized
as follows. The continuous flow theory envisions the total phosphorus to be
washed from the land, through the river system, and into the receiving water
body during one storm event. The discontinuous theory would propose that the
phosphorus is moved from the land and through the stream by a series of flood
waves. The first wave would carry the material from the land into the river
bed. The second wave would pick up the total phosphorus, carry it some
distance, and redeposit it in the river again. This process would continue
until the total phosphorus reaches the receiving water body. By either
transport scheme the total phosphorus originates from the land surface and
ends in the receiving water body.

The goal of this research is to determine which of the two theories is the
more plausible. The methodology to be employed is to derive mass balances
for the water and the total phosphorus, to use these models to simulate the
transport of total phosphorus in a river system with inflow and sometimes
with a resuspension input, and to compare the results of these simulations
with the known characteristics of total phosphorus concentrations and flow
rates during storms in the rivers of western Ohio. If the simulation with
inflow alone correctly predicts the hydrograph and chemograph charac-
teristics, the effect of resuspension of total phosphorus from the sediments
will be assumed negligible. However, if only the resuspension mechanism is
capable of generating the required characteristics of the measured che-
mograph, then it will be presumed that this mechanism is prime means by which
total phosphorus is transported.

Observed Data From Rivers

Figure 1 contains a plot of river flow rate and total phosphorus con-
centration as a function of time for Tymochtee Creek which is a tributary of
the Sandusky River. Several characteristics of this chemograph and
hydrograph are typical of all such chemographs and hydrographs measured in
the Sandusky, Portage, Maumee, and Huron Rivers of western Ohio. These
characteristics are: (1) the peak of the total phosphorus concentration
almost always leads the flow rate peak of the river at any station, (2) the
total phosphorus concentration declines to its low flow value before the flow
returns to its approximate steady flow range of values, and (3) the peak
total phosphorus concentration is not necessarily higher at the downstream
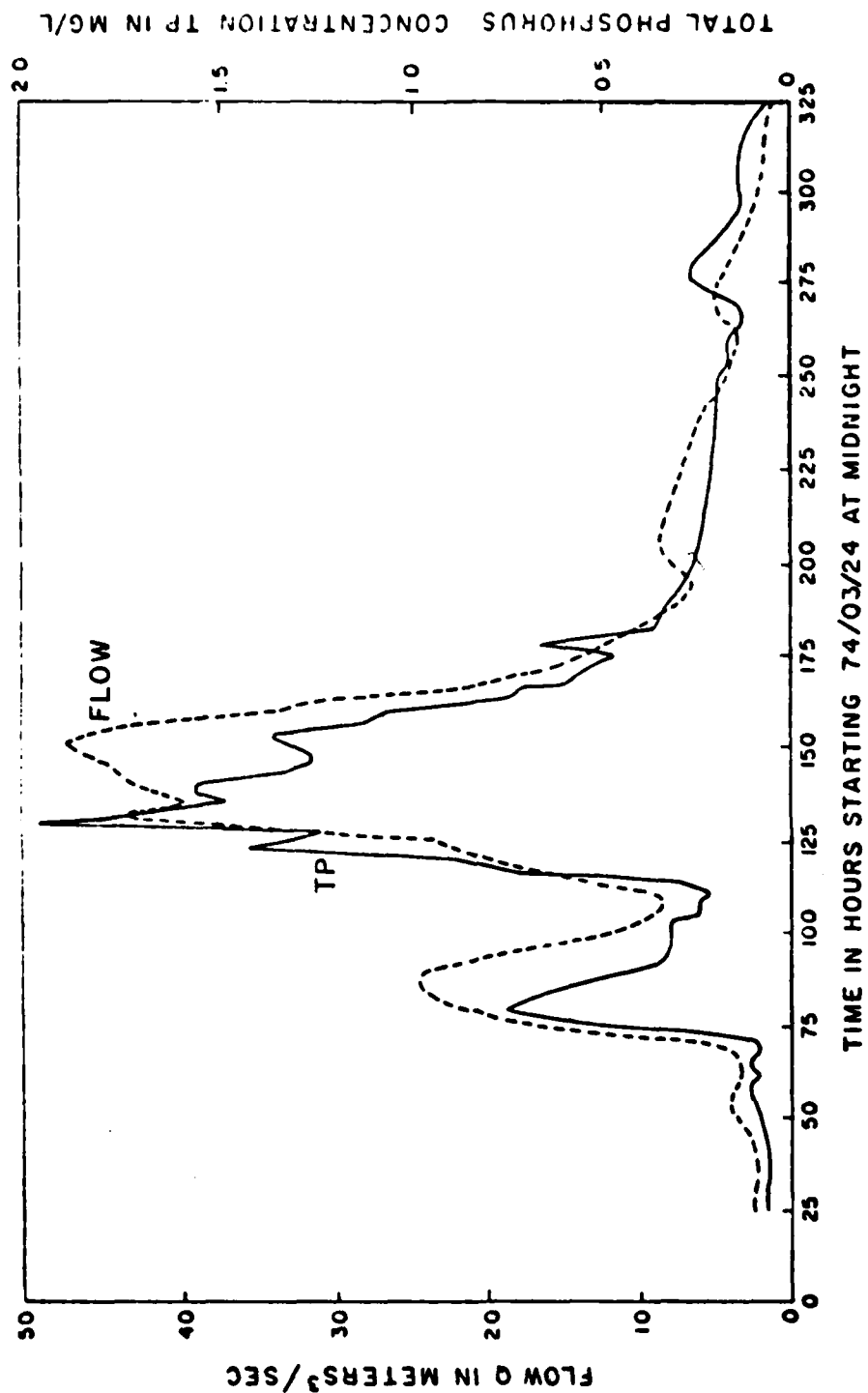stations than at the upstream stations.

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Fig. 1. - Hydrograph and chemograph at the U.S.G.S. gaging station on Tymochtee Creek at Crawford, Ohio

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These three characteristics will be used to discern the correctness of the two different theories for phosphorus transport in river reaches.

Mass Balance Model

The mass balance model used to simulate the hydrograph is the differential mass balance over an increment in the axial direction and an increment in time.

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = q$$

where
- A = discharge area of the stream
- Q = volumetric flow rate of the stream
- q = influx volume rate per axial distance
- x = axial variable
- t = time

This equation contains two dependent variables, A and Q. In order to solve this equation, another relationship between these two variables must be found; usually it is a force balance over an infinitesimal axial distance and time. However, to simplify simulation, the rating curve (flow as function of stage) will be formulated such that Q, flow rate, is a function of A, stream discharge area. The normal dispersion term in the force and mass balances will be absent from this formulation: however, dispersion will not affect any of the characteristics of hydrograph and chemograph with which a comparison will be made since dispersion will not change the position of the total phosphorus peak and will tend to spread the phosphorus peak.

The relationship between the discharge and area is determined from field data and typical curves for the Sandusky River are shown in Figure 2. The relationship between Q and A is similar for all four stations. The influence of water slope on this relationship has been shown to be negligible. Calculations indicate that the flow is about four percent higher during the rising stage than that predicted by the Q vs. A curve.

Two different formulations of the mass balance are required for this study. One considers only the inflow and transport of total phosphorus and is derived from a mass balance on total phosphorus for an incremental distance and incremental time in the stream.

$$\frac{\partial AC}{\partial t} + \frac{\partial QC}{\partial x} = qC_i$$

or expanding

$$A\frac{\partial C}{\partial t} + Q\frac{\partial C}{\partial x} + qC = qC_i$$
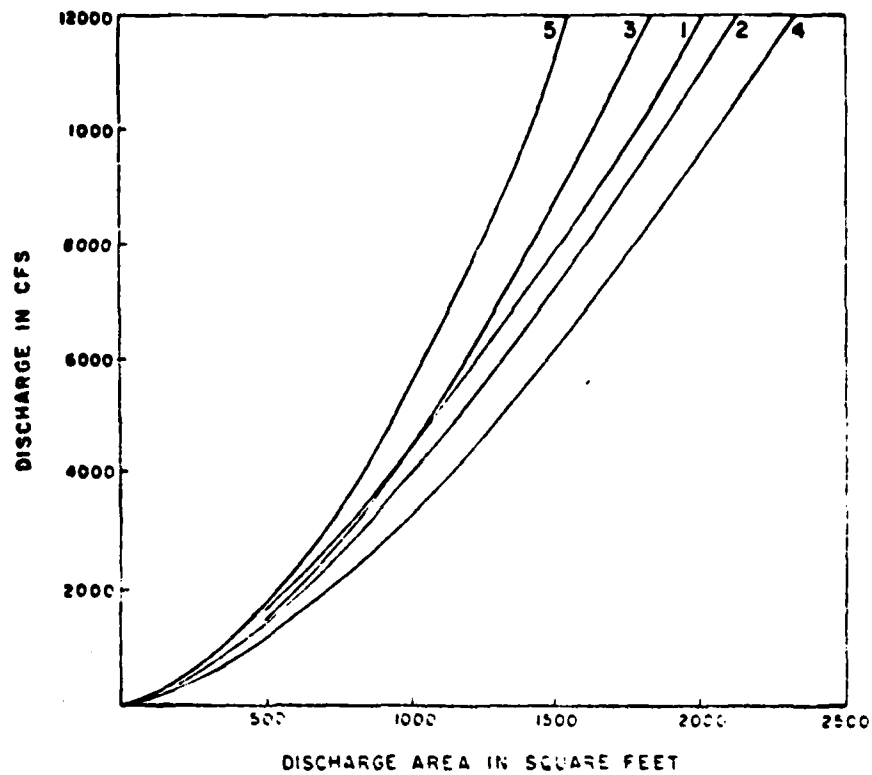
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Fig. 2. - Discharge vs. area curves for stations
in the Sandusky River basin at U.S.G.S. gaging
stations: 1 = Sandusky River near Bucyrus;
2 = Sandusky River near Upper Sandusky; 3 =
Tymochtee Creek at Crawford; 4 = Sandusky River near
Mexico; 5 = Sandusky River near Fremont

where

C = concentration of total phosphorus in the stream
C_i = concentration of total phosphorus in the influx flow

For the case of significant resuspension and deposition of total phosphorus during flow the mass balance takes the following form.

$$A\frac{\partial C}{\partial t} + Q\frac{\partial C}{\partial x} + qC = qC_i + \propto \frac{\partial u}{\partial t} C$$

where

u = velocity in the stream
$\propto$ = proportionality constant

The resuspension and deposition phenomena is presumed to be dependent upon the rate of change of velocity with time. Thus when the velocity is increasing there is a net input into the water column and when the velocity is decreasing there is a deposition from the water. Although the functional form of this phenomena may be different than that proposed, the general characteristics are similar to what actually is occurring in the stream. The coefficient, , can be varied to obtain reasonable total phosphorus concentration profiles.

Because of the variability of q and the desire to introduce some dispersion, the equations were solved numerically. The hydrographs and chemographs that are calculated are derived from information obtained at one point in the river and hence the assumption that the whole stretch of river is similar to the measured point is implied. The finite difference approximation for the water balance is shown below.

$$A_{i+1,j+1} = \frac{A_{i+1,j} + A_{i,j+1} \; f'\frac{\Delta t}{\Delta x} + q\Delta t}{1 + f'\frac{\Delta t}{\Delta x}}$$

where

f = function of A and defines Q
f' = derivitive of f

Results of the Simulation

All the simulations were started with steady state stream conditions with respect to flow and concentration. The input hydrograph and chemograph are shown in Figure 3(a). The results in Figure 3(b) indicate that after 40

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Fig. 3. – Model results: a) initial conditions;
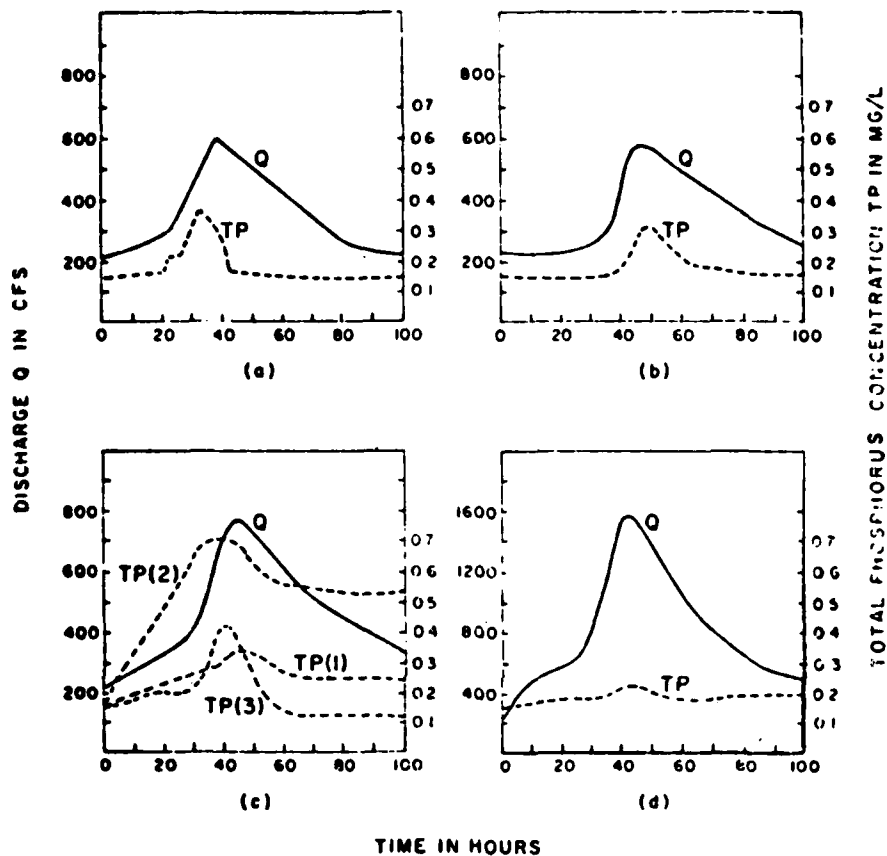b) distance downstream = 40 miles, no inputs;
c) distance downstream = 40 miles, local inflow =
0.02 x Q cfs/mile, local total phosphorus inflow
concentration, TP(1) = 0.375 mg/l, TP(2) =
1.015 mg/l, TP(3) = 0.1875 mg/l with resuspension/
deposition; d) distance downstream = 40 miles,
local inflow = 0.1 x Q cfs/mile, local total
phosphorus concentration = 0.1875 mg/l

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miles downstream with no water or chemical input, the peak of total
phosphorus has moved behind the peak of water flow. Note that the numerical
methods introduce some dispersion into the system.

Figure 3(c) contains the plot of the output hydrograph and several related
chemographs for the condition in which the inflow rate was equal to two per-
cent of the upstream flow rate per mile. When the inflow total phosphorus
concentration was equal to the initial peak concentration, the peak in the
total phosphorus concentration lagged behind the hydrograph peak and the
total phosphorus concentration did not return to the low flow value within
the time frame of the hydrograph. This is not in agreement with observed
facts. The total phosphorus concentration peak did remain ahead of the
hydrograph peak for input concentrations equal to three times the initial
peak concentration; however, in contrast to field observations the con-
centration did not decline with the decline in the hydrograph and the peak of
concentration constantly increased as the flood wave moded downstream.
Figure 3(d) exhibits the hydrograph and chemograph for an increased input
flow rate. Again the total phosphorus peak falls behind the water peak and
the inflow is so large that the total phosphorus is diluted. Many other
inputs were considered and none yielded results which were in conformity with
reality.

Only when the resuspension and deposition term was included in the total
phosphorus mass balance did the downstream hydrograph and chemograph possess
the observed field characteristics as shown in Figure 3(c). The peak in
total phosphorus concentration remained ahead of the hydrograph peak and the
total phosphorus concentration declined with the declining hydrograph. The
peak of total phosphorus concentration did not necessarily increase
downstream but its variability depended upon the value of the constant, ,
in the resuspension functionality.

The relative position of the total phosphorus peak, to the discharge peak is
shown in Figure 4. Almost all conditions which were simulated with only
total phosphorus input resulted in the total phosphorus peak eventually
lagging behind the flow peak. If the input concentration were made large
enough, the total phosphorus peak would approach the water peak and then move
ahead again. Only when the resuspension term was included did the relative
position of total phosphorus peak to the water peak remain stationary.

Conclusion and Summary

The flow of water and total phosphorus was simulated in a stream with dif-
ferent types of total phosphorus transport mechanisms. The results of the
simulations were compared with known properties of observed hydrographs and
chemographs. It is concluded that the major mechanism required to explain
the observed results is one which postulates the resuspension and deposition
of total phosphorus from the reaches of the river. Thus most of the total
phosphorus moves through a river reach by moving a finite distance with each
high flow event passing through the river.

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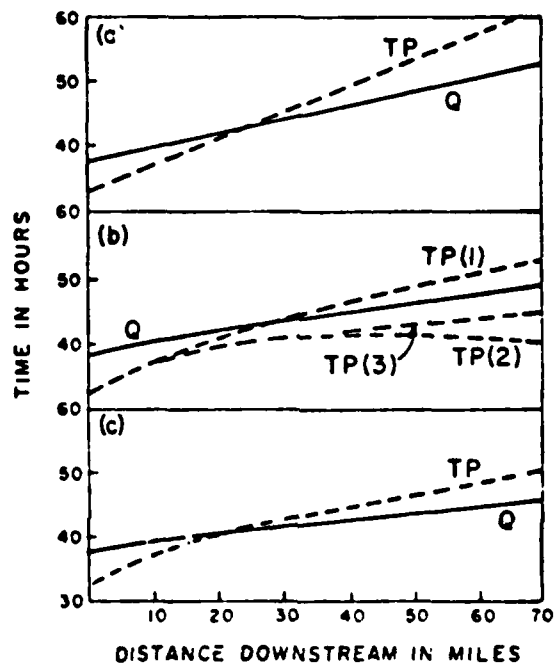
Fig. 4. - Time vs. distance downstream of the hydrograph and chemograph peaks; a) no inflow conditions; b) local inflow = 0.02 x Q cfs/mile, local total phosphorus concentration, TP(1) = 0.375 mg/1, TP(2) = 1.015 mg/1, TP(3) = 0.1875 mg/1 with resuspension/deposition; c) local inflow = 0.1 x Q cfs/mile, local total phosphorus concentration = 0.1875 mg/1

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STORM TRAVEL DISTANCE CALCULATIONS
FOR TOTAL PHOSPHORUS AND SUSPENDED
MATERIALS IN RIVERS

by

Frank H. Verhoff
Department of Chemical Engineering
West Virginia University
Morgantown, West Virginia   26505

and
David A. Melfi
and
Stephen M. Yaksich
Lake Erie Wastewater Management Study
U. S. Army Corps of Engineers
Buffalo, New York   14207

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Abstract

From previous work it appears that total phosphorus is transported through rivers by a series of storm events. This paper presents a method for calculating the average distance of travel during any given storm event. The method uses the hydrograph, chemograph, and flow characteristics at a point in the river. Comparisons were made between storm events at the same station in a river, between different stations in the same river basin, and between stations in different rivers. Results show the distance of travel is dependent upon the magnitude and duration of the storm event, but not on the magnitude of the total phosphorus concentration.

Introduction

Most of the total phosphorus in streams appears to be transported during storm events and is associated with suspended solids transport. Several other pollutants such as some pesticides are also transported in conjunction with the suspended material. Materials transported in this manner exhibit several characteristics. The concentration of the total phosphorus, suspended solids, etc. increases with increasing discharge (see U. S. Army Corps of Engineers (1975), Walling (1977), Verhoff, Melfi, and Yaksich (1978)). Also during any storm event the peak in total phosphorus or suspended solids concentration occurs before the peak in discharge. Verhoff and Melfi (1978) have used these facts to show that total phosphorus is transported from the land surface to the receiving water body by a series of storm events. Each storm event picks up the total phosphorus from the stream bottom, banks, and flood plains, transports it some distance downstream, and deposits it in the stream again. This mechanism was suggested by Keup (1968) and again discussed by an Enviro Control Report (1972).

A major question to be answered concerning this mechanism is what is the average distance of travel for the total phosphorus during any given storm event. This question is also an important one in sediment transport. M.G. Wolman (1977) discusses the various aspects of sediment transport including the wash load, the bed load, and the many complications related to yield. In his introductory paragraph he cites the ruling of Judge R. H. Kroninger in a controversy over logging in a redwood forest. The Judge writes, "While numerous expert witnesses in the fields of geology, forestry, engineering, and biology were presented, their conclusions and the opinions they derived from them are hopelessly irreconcilable on such critical questions as how much and how far solid particles will be moved by any given flow of surface water. They were able to agree only that sediment will not be transported upstream" (State of California, Marin County, versus E. Righetti et.al., (1969)). This paper will discuss the critical question of travel distance. A method for the calculation of distance of travel for total phosphorus and suspended solids for a given flow of surface water will be presented. A previous paper (Verhoff, Melfi, and Yaksich (1978)) discusses the calculation of the amount of total phosphorus transported past a given point in a stream. Both of these techniques are based upon data taken from that point in the stream.

Little prior work has been done in trying to understand the intermittent transport of total phosphorus; however, there have been many papers written on the subject of suspended solids transport. Nordin divides the modeling efforts into two categories; (1) sediment movement modeled by computational deterministic hydrology (e.g. Bennett (1974), Bagnold (1977), and Thomas K. Prasuhn (1977)); and (2) stochastic models used to simulate the movement of particles (e.g., Cheong and Shen (1976), and Todorovic and Nordin (1975)). These efforts have followed the same basic procedure. First, the deterministic model is proposed based upon force balances or the stochastic model is proposed based upon some jump probabilities. The predictions of these models are then compared with experimental data to assess the accuracy of the original proposed models.

The work to be discussed in this paper does not start with a proposed model for total phosphorus transport and compare results with experimental data. Rather the procedures start with the experimental data and use mass and force balances to calculate what must have happened to the total phosphorus to achieve the given data. From these calcu-lations, estimates of the probability distribution, the average distance of travel, and the variance of the travel distance can be calculated.

The method is based upon the data from a stream at one point and hence is good only at that point. However, many streams do not change significantly for long distances and thus the procedure can imply information for more than just a point in a stream. The data needed for the computational scheme is the river flow rate and the total phosphorus concentration (suspended solids concentration) as a function of time for the chosen point in the stream. Further, the river discharge as a function of the cross sectional area at the same point in the river is required. The mass balance is applied to this data to obtain the desired information.

Methodology

From the previous work it has been suggested that the transport of total phosphorus occurs via a mechanism by which the phosphorus is picked up at one point in the stream and deposited at another. This conclusion results from two facts. First, the time dependency of the total phosphorus concentration closely resembles the dependency of the suspended solids which are transported by the same mechanism. Second, the peak of the total phosphorus concentration generally precedes the discharge peak. If the total phosphorus were carried by the water itself, the peak concentration would gradually fall behind the discharge peak because the water velocity is slower than the wave celerity.

Given that the total phosphorus is transported from one point in the stream to another, the distance of transport becomes an important issue as was discussed previously. With considerable effort this distance of travel could possibly be measured experimentally for any given reach of stream by employing tracer particles. However, these distance estimates would be valid only for particles with characteristics similar to the tracer and only for the individual stretch. Numerous measurements would have to be made for different particle sizes and different stream reaches just to understand one river basin. This same information can be estimated quite simply from the hydrograph and chemograph measured at a given point in a stream.

The technique to be described uses the assumption that the water is moving as a kinematic wave. Further, the actual distances calculated are derived from information obtained at one point in the river and hence the assumption that a given reach of river is similar to the measurement point is implied.

The calculational procedure is based upon two data sets; the time dependency of both flow and total phosphorus concentration and the flow versus area curve for the rated point in the stream. Figure 1 illustrates a typical river discharge and total phosphorus concentration as a function of time for a given point in the river. Notice that the total phosphorus concentration peaks before the water flow rate. Figure 2 contains the water flow rate as a function of the cross sectional area of flow for various points in the river.
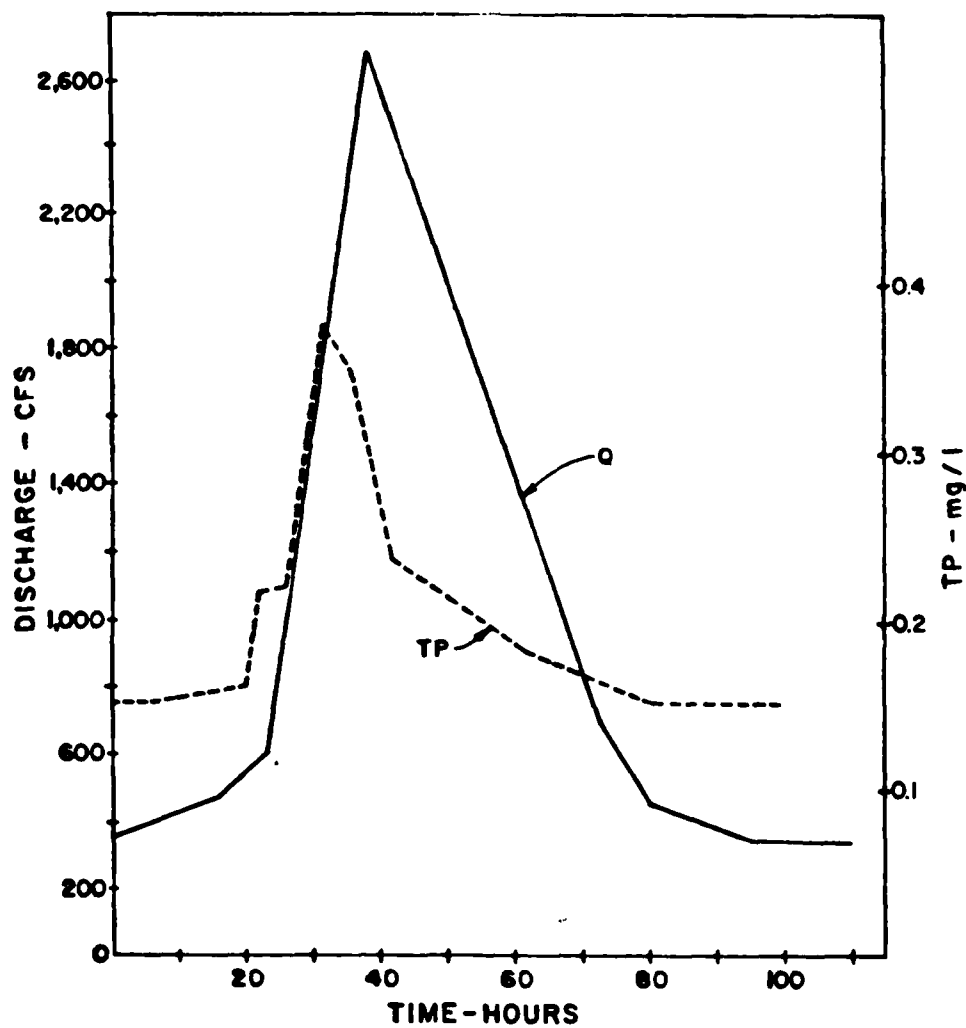
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Figure 1 - Hydrograph and chemograph (total phosphorus) for the Sandusky River near Fremont, Ohio, for the storm of 7 December 1974.
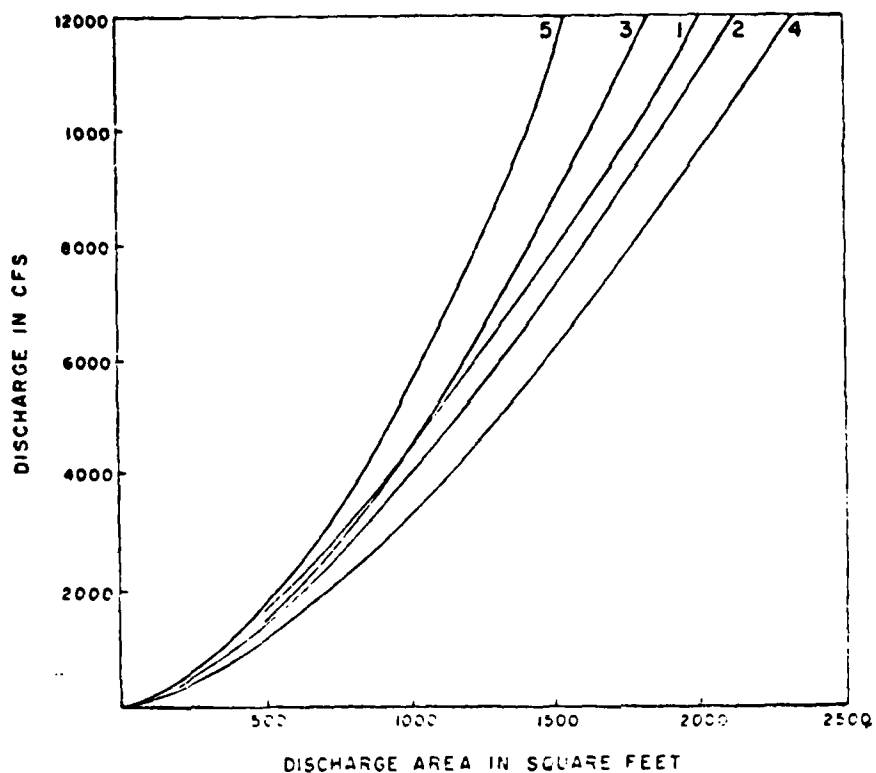
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Figure 2. - Discharge vs. area curves for stations
in the Sandusky River basin at USGS gaging
stations: 1 = Sandusky River near Bucyrus;
2 = Sandusky River near Upper Sandusky; 3 =
Tymochtee Creek at Crawford; 4 = Sandusky River near
Mexico; 5 = Sandusky River near Fremont.

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The kinematic wave theory for river flow indicates that the wave moves faster downstream than the water itself for subcritical flow. Hence, if the information contained in Figure 1 was also measured at an incremental distance downstream, it would appear approximately the same except that the water itself would be slightly shifted in the hydrograph because of its slower velocity than the wave celerity. Since the water itself is moving slower than the wave, a particular volume of water would appear to be moving from left to right through the hydrograph and chemograph shown in Figure 1 as this wave proceeds downstream. As a volume of water moves through the hydrograph, the total phosphorus concentration of this water gradually increases as material is picked from the river banks and bottom and after the concentration peak is reached the concentration decreases again as this material is deposited. Thus, if the position of the volume of water in the hydrograph could be related to its position in the stream, it would be possible to determine the total phosphorus concentration of the volume of water as a function of distance downstream (see Figure 3).

To obtain these necessary relationships, the flow versus cross-sectional area curve is employed. This relationship is plotted in Figure 2 and can be represented by the following equation.

$$Q = g(A) \tag{1}$$

where Q = river flow rate
A = cross-sectional area

According to the kinematic theory of hydrologic events, the wave celerity is quantitatively determined by the slope of the curve, and the velocity of the water itself is found by dividing the flow rate by the area. The water and wave velocities are indicated in Figure 3.

$$v_w = g'(A) \tag{2}$$
$$v = g(A)/A \tag{3}$$

where v = water velocity
v_w = wave celerity

Now for any time increment, the incremental distance traversed by the water volume is determined by the water velocity as shown below.

$$ds/dt = v \tag{4}$$

where s = distance downstream of water volume
t = real time

However, as the distance downstream of the water volume, s, changes the position of the water in the hydrograph shifts. The problem is to relate the position in the hydrograph of the given volume of water with the distance downstream that the water has moved.
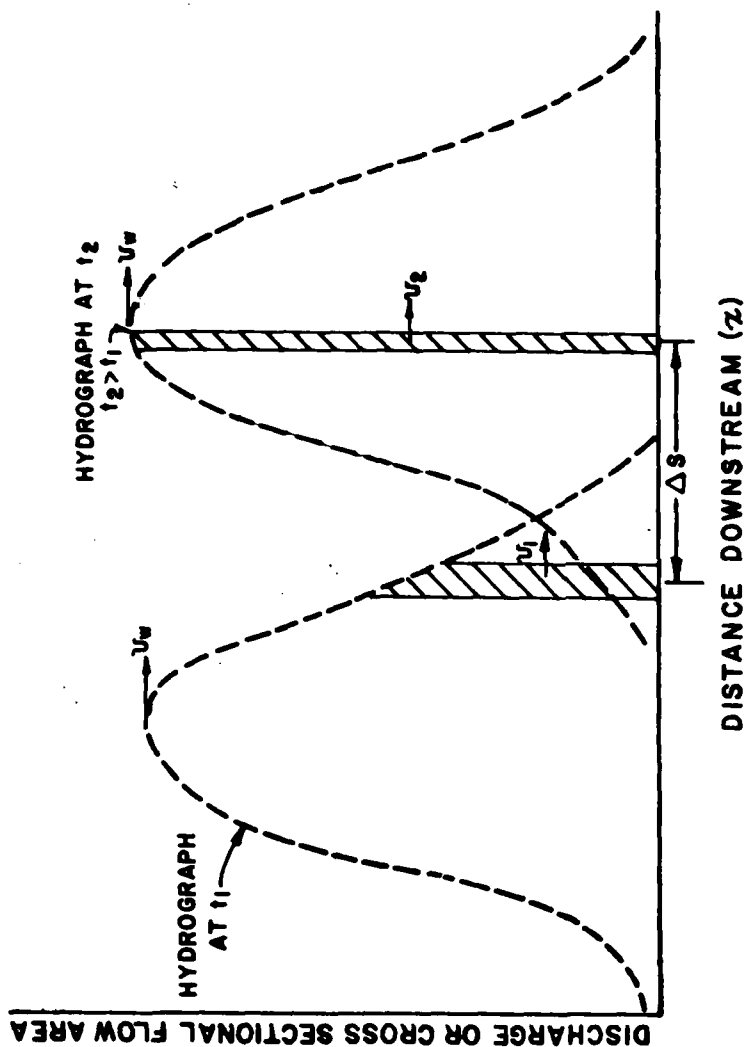
Figure 3 – A plot of area or discharge as a function of axial river distance showing the storm wave at two different times with the associated position of a water parcel. V_1, V_2 = Water Velocity V_w = Wave Velocity

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To obtain the desired relationship it is necessary to consider the dynamics of a wave form in a river. If only short distances are considered such that no appreciable change in the hydrograph shape has occurred this wave form satisfies the following relationship. This implies the wave velocity is approximately constant and that there is little inflow into the stream. These assumptions are usually reasonable since the wave velocity, dQ/dA, is nearly constant for high flows and tributary input is not considered.

$$f (t_o - X/v_w) = C \qquad (5)$$

where C = constant
t_o = time
X = axial coordinate downstream

This equation states that if an observer is moving at the velocity of the wave, there will be no change in the hydrograph at the observation point. If the observer is not moving with the wave, then a positive change in the variable t_o is equivalent to a positive change in the variable X/v_w. This can be written in differential form as the following equation assuming v_w is nearly constant.

$$dt_o = dX/v_w \qquad (6)$$

To perform the desired transformation as discussed above, it is necessary to consider the change in position of a given parcel of water relative to the wave as the wave proceeds downstream.

$$dX/dt = v_w - v \qquad (7)$$

where X = axial position of water parcel relative to the wave

This then can be transformed into a time into the hydrograph by using the properties of waves discussed above.

$$\frac{dX/v_w}{dt} = \frac{dt_o}{dt} = 1 - v/v_w \qquad (8)$$

This differential equation then relates the time into the hydrograph to real time during the water movement downstream. It is then a simple matter of relating the position of the water parcel downstream to its position in the hydrograph.

$$\frac{ds}{dt} = \frac{ds}{dt_o} \frac{dt_o}{dt} = v \qquad (9)$$

or
$$\frac{ds}{dt_o} = \frac{v v_w}{v_w - v} = \frac{1}{\frac{1}{v} - \frac{1}{v_w}} \qquad (10)$$

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or
$$\frac{ds}{dt_0} = \frac{g'(A)\ g(A)}{g'(A)A - g(A)} \tag{11}$$

This differential equation then relates the distance traversed by the parcel of water downstream to its position in the hydrograph as designated by time into the hydrograph. But from the hydrograph and chemograph data the total phosphorus concentration is also known as a function of time into the hydrograph. Thus by integrating the differential equation from some zero distance at the beginning of an event in the hydrograph, it is possible to obtain the concentration of total phosphorus in a given parcel of water as a function of the distance that parcel has traveled downstream. This can be represented by the following relationship.

$$C_{TP} = C_{TP}(s) \tag{12}$$

where C_{TP} = total phosphorus concentration

A typical example of the relationship is shown in Figure 4. This figure indicates that as the particular volume of water enters the hydrograph, its total phosphorus concentration increases indicating there is a net resuspension of material presumably from the material in contact with the water. At a certain point downstream, the total phosphorus concentration reaches a maximum and further progression downstream causes the net total phosphorus of the given volume of water to be reduced. Presumably during this time period the material is being deposited along the banks and the stream bottom.

The information in Figure 4 can be used to calculate the average distance that the total phosphorus has been moved downstream during a given hydrological event. To help understand the process, a simple example will be discussed. Figure 5a illustrates a graph of C_{TP} versus downstream distance in which the transport distance is obviously S_0. A more complicated example is depicted in Figure 5b. The average distance traversed by the total phosphorus concentration is given by the following formula.

$$S_{av} = \frac{S_0 C_0 + S_1 C_1}{C_0 + C_1} \tag{13}$$

This equation can be generalized for the curve shown in Fig. 4. The formula to be employed is as follows.

$$\bar{s} = S_{av} = \frac{\int_{C_{min}}^{C_{max}} s\,dc}{\int_{C_{min}}^{C_{max}} dc} = \frac{\int_{S_{min}}^{S_{max}} c\,ds}{C_{max} - C_{min}} \tag{14}$$
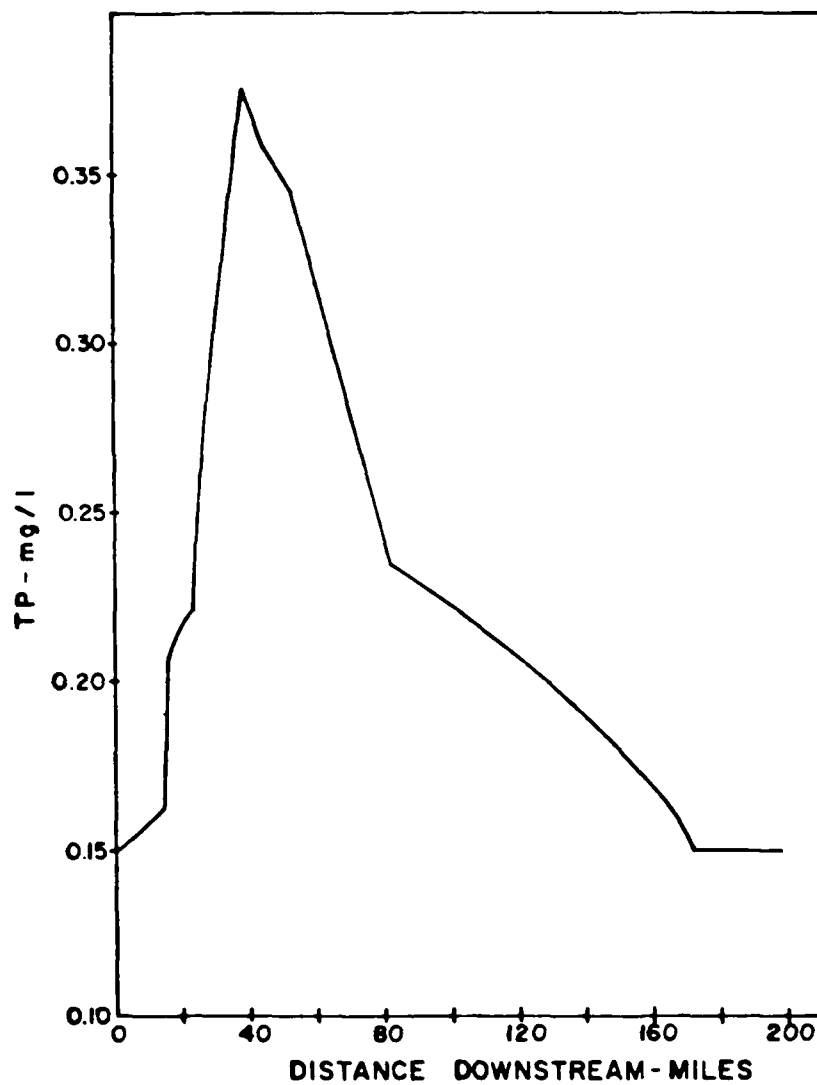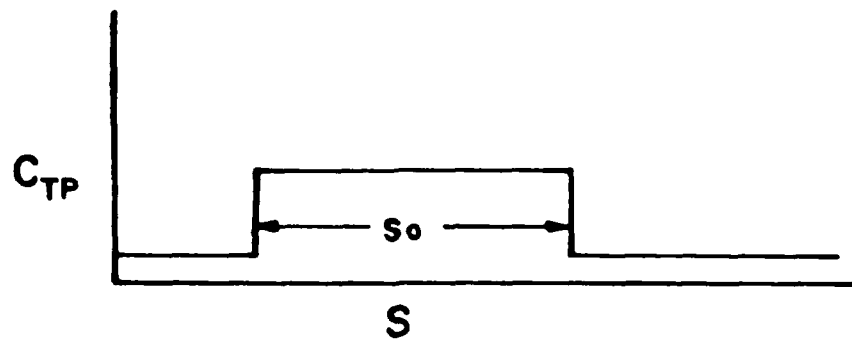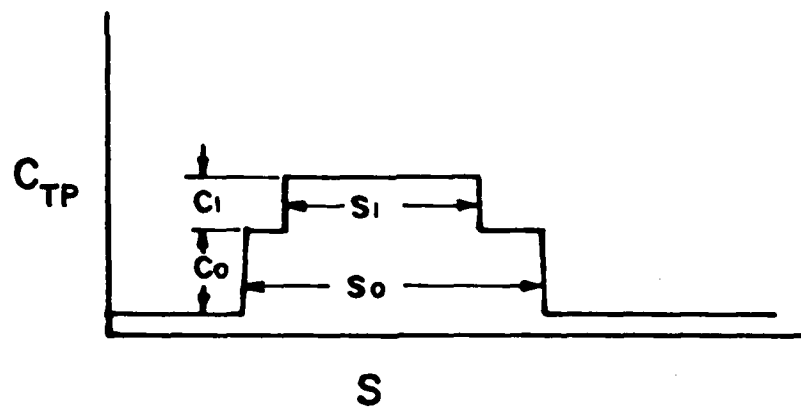
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Figure 4 - Total phosphorus concentration in a
water parcel as a function of water parcel
travel distance for the storm of 7 December 1974
at Fremont, Ohio.

(a)

(b)

Figure 5 - Illustrations of the average travel distance for total phosphorus.

In a similar manner the variance can be calculated by the following formula.

$$\sigma_s^2 = \frac{\int_{C_{min}}^{C_{max}} (s-\bar{s})^2 \, dc}{C_{max} - C_{min}} \tag{15}$$

Further, the probability density function for total phosphorus travel distance can be calculated. This is accomplished by dividing the total phosporus concentration curve versus the distance downstream into portions as is shown in Figure 6. The probability for each of the indicated increments in s is proportional to the increment in the total phosphorus concentration divided by the total increment in total phosphorus concentration. The equation below represents this mathematically.

$$P_i = P(\wedge s_i) = \wedge C_i / \wedge C_t \tag{16}$$

These calculated quantities can then be used to plot the probability density function.

Application to the Sandusky River in Ohio

The above described procedure will be applied to several points in the Sandusky River basin in Ohio. All the information needed was measured and plotted as illustrated in Figures 1 and 2. This information could be used numerically or equations could be fit to the data and the manipulations could be performed algebraically, or a combination of algebraic and numerical techniques could be employed.

One approximation scheme which greatly simplifies the computations is to assume the Q vs A curve to be linear in the region of interest. This is a good assumption considering the fact that this curve is nearly linear in the high flow section which is needed during storm events and consequently, the wave velocity is constant. Thus, the curve can be approximated by

$$Q = bA - a \tag{17}$$

Substituting this into Eq. 11 yields the following simple expression to solve

$$ds/dt_o = (b/a)Q \tag{18}$$

To use this expression it is necessary to measure the slope, b, of the Q vs A curves and its intercept, a, over the region of flow occurring during the storm event of interest. Starting with the water parcel at any point in the hydrograph t_o , and a point in the stream, s_i, the area under the (b/a) Q curve between t_o and t_i determines the distance moved by the water parcel $(s-s_i)$.

The water parcel at any point in the hydrograph has associated with it a total phosphorus concentration and a distance downstream. Thus the total phosphorus concentration can be plotted as a function of distance downstream.
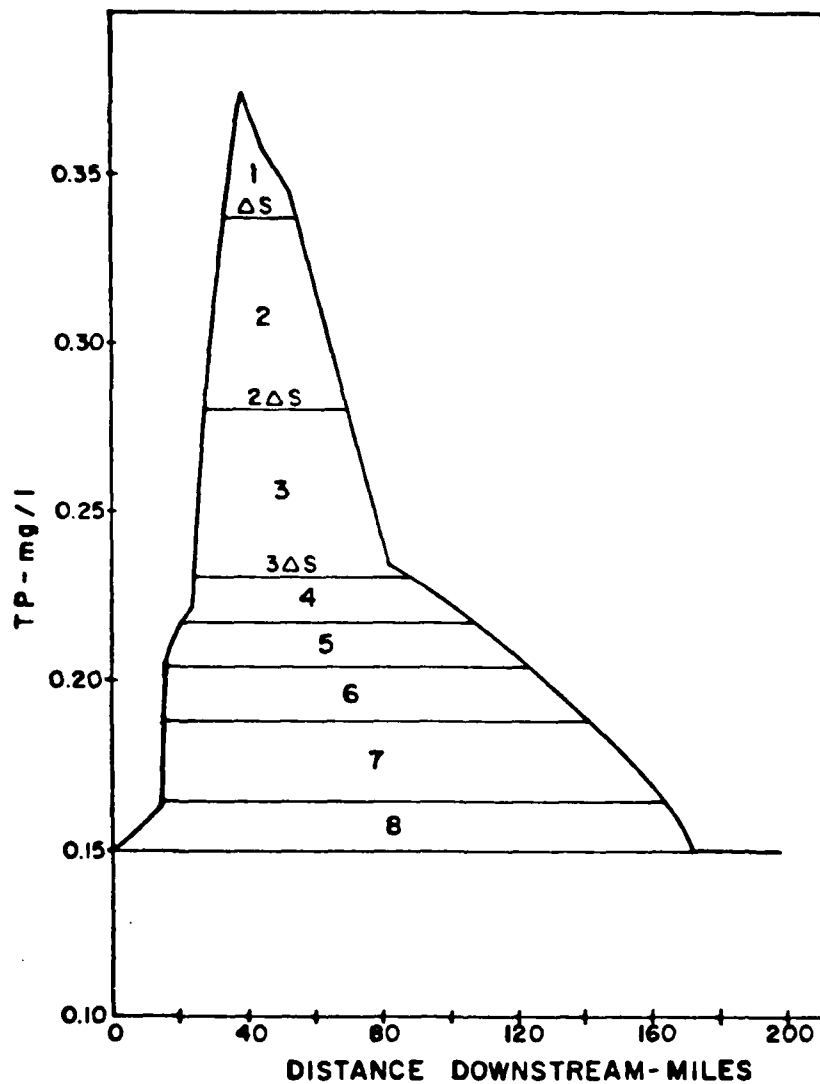
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Figure 6 - Graphical construction for the
calculation of distribution of total
phosphorus travel distances from the total
phosphorus chemograph.

These procedures were applied to the information shown in Figure 1 for the Sandusky River at Fremont. The Q vs A curve for Fremont from Figure 2 was used and the resulting total phosphorus concentration as a function of distance is shown in Figure 4.

The average net distance of travel and the variance of this travel then can be calculated using Eqs. 14 and 15. For this point in the stream the average net distance of travel was 64 miles and the stan dard deviation for this travel was 45 miles. The stream with the characteristic Q vs A curve at Fremont was transporting the total phosphorus an average distance of 64 miles as the storm was passing that point. It must be emphasized that these calculated values only apply at the measurement point.

Further then, the probability distribution of distance transported can be calculated. Figure 6 demonstrates the construction procedures required to obtain the approximate distance of travel. The resulting probability distribution is shown in Figure 7. This probability distribution was typical of the several which were calculated. In some instances it appeared that distribution definitely had two peaks and in others the distribution looked Poisson in nature. Given that the distribution is bi-modal, it is possible to speculate that two different total phosphorus transport mechanisms are operative. One fraction of total phosphorus may be absorbed to dense clay particles and have a short travel distance. Other total phosphorus may be associated with less dense biological materials such as bacterial or fungal cells and these may be transported greater distances.

In some previous work, the yearly flux of total phosphorus from the Sandusky River into Lake Erie was calculated using the measurements at Fremont. It was presumed that all of the material passing Fremont went into Lake Erie 15 miles away. The probability distribution in Figure 7 indicates that about 90 percent of the material will be transported this distance if the river remains similar to the flow characteristics at Fremont. Since the river probably resuspends some material in the last 15 miles, the estimate of total flux obtained at Fremont probably is reasonable for that entering the lake.

The important point to note is that the computations apply only at a point. However, points in a stream can differ in two regards, in the Q vs A curve or in the hydrograph and chemograph. Figure 2 shows the Q vs A curve at various stations on the Sandusky River. There are no great differences in these curves and hence the major differences must lie in the hydrograph and chemograph.

This travel distance estimation procedure was applied at several other stations in the Sandusky River Basin for the storm of 7 December 1974. The cumulative distributions of distance traveled is shown in Figure 8. It can be seen that for this storm, three main stem Sandusky River stations at Fremont, Bucyrus, and Upper Sandusky all give approximately the same distribution of travel. Only the station at Mexico yields a significantly greater distance of travel. This primarily results from a different chemograph, which may have been influenced by the dam upstream from the Mexico station. Further, the distance of travel at Crawford on Tymochtee Creek, a tributary of the Sandusky River, is significantly less than for the main stem reaches.
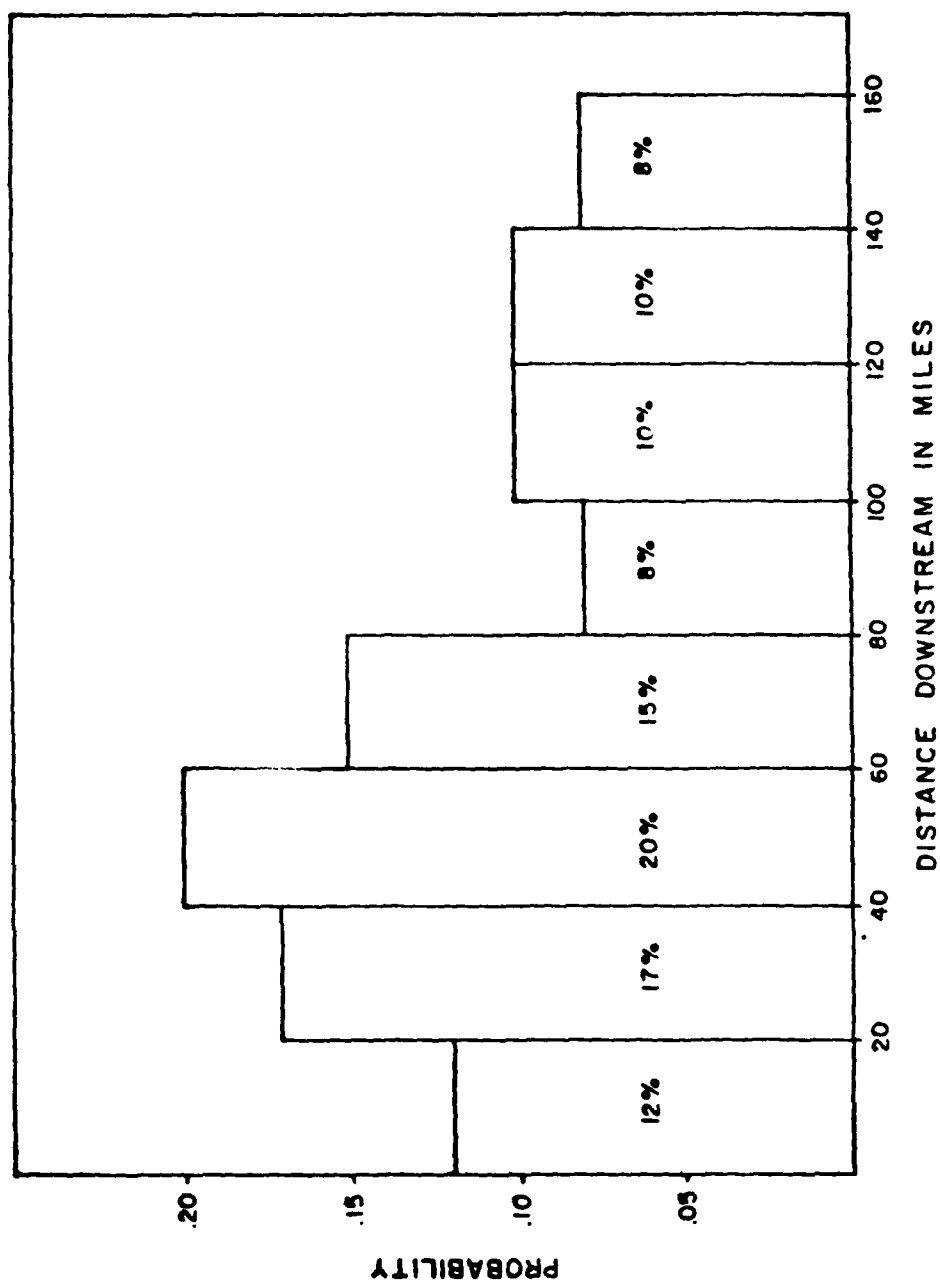
Figure 7 - Distribution of travel distances for total phosphorus in the Sandusky River at Fremont for the storm of 7 December 1974.
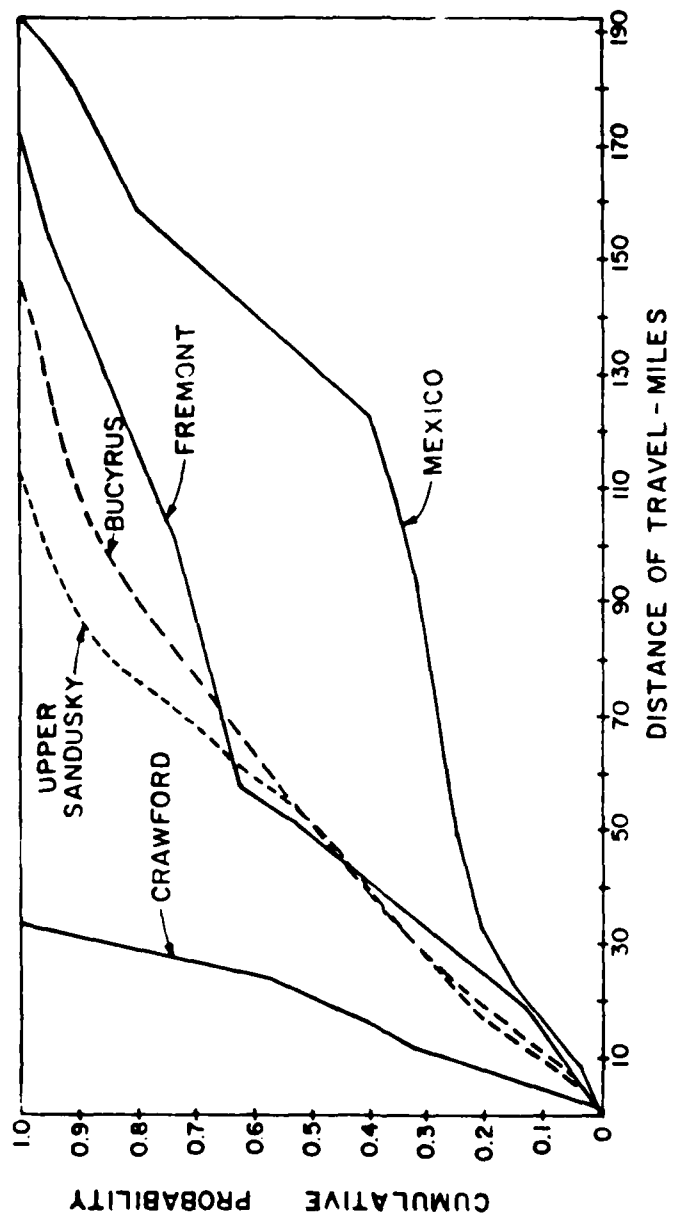
Figure 8 – Cumulative probability of travel distances at various stations in the Sandusky River basin for the storm of 7 Dec 1974.

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It appears that in the upper reaches of river basins the distance of travel might be much shorter because the duration of the hydrograph is much less.

The travel distances were calculated for another much larger storm on the Sandusky River. The average travel distances were correspondingly larger. At Fremont on the Sandusky River with a maximum flow of 15,000 cfs for the storm of 22 February 1975 the travel distance was 2,256 miles. Since Fremont is 15 miles from Lake Erie, almost all of the total phosphorus measured passing Fremont gets into Lake Erie. In order to show that the actual magnitude of the total phosphorus concentration has little effect on the distance of travel, the calculations were performed for this same storm with exactly one-half of the concentration. The average distance of travel is 2,257 miles. However, the magnitude of the concentration directly affects the amount of transport. In contrast, the magnitude of the water flow rate has a significant effect on the distance of travel.

This calculation procedure was performed for storm events on the Maumee River and the Cattaraugus Creek in the Lake Erie basin. The average distance of travel for three different storms on the Maumee River at Waterville were 403, 470, and 1,161 miles and the associated maximum flow was 18,700, 31,200, and 50,400 cfs, respectively. This result indicates that the distance of travel increases with increasing maximum flow for a given station. The storm of 29 January 1975 on the Cattaraugus Creek had a maximum flow rate of 15,000 cfs yet the distance of travel for total phosphorus was only 49 miles. The Cattaraugus Creek Basin has a much higher slope and the stream events have a shorter duration; thus it would appear that short duration storm events produce smaller travel distances for the total phosphorus. This again corroborates the measurements at Crawford in Tymochtee Creek.

Summary and Conclusions

In this paper is developed a calculational procedure for estimating the distance of travel for total phosphorus, suspended sediment, and other associated materials. The procedure is based upon the characteristics of the stream at a point and requires a knowledge of the hydrograph and the chemograph for the substance of interest. Further, the river flow as a function of river cross sectional area is needed for the point in the stream.

The calculational procedure is based upon the difference in the wave celerity and the water velocity. The calculated distances of travel for total phosphorus appear to be reasonable. This calculation for distance of travel is far simpler than any experimental technique which could be devised to obtain the same information.

The distance of travel for total phosphorus was calculated at various points on the Sandusky and Maumee Rivers, and Cattaraugus Creek. The distance of travel increases with increasing maximum flow rate at a given point in the stream and it increases with increasing storm duration. For a given storm event the distance of travel in the upper reaches of a tributary is less than at the main stem stations. The channel slope apparently influences distance of travel. Finally such stream alterations such as dams or channeling also influence the distance of travel for total phosphorus.

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MOMENT METHODS FOR ANALYZING RIVER MODELS
WITH APPLICATION TO POINT SOURCE PHOSPHORUS

by

F.H. Verhoff
Department of Chemical Engineering
West Virginia University
Morgantown, WV   26506

and

David B. Baker
Water Quality Laboratory
Heidelberg College
Tiffin, OH   44156

Abstract

Quantitive analysis of the fate of point source pollutants in streams can be
achieved by using moment analysis if the input concentration is periodic.
The moment analysis permits the discrimination among various proposed models
and permits the estimation of the parameters in the selected model for
describing the fate of the substance in a river.

Ortho phosphorus enters the Sandusky River from the Bucyrus, Ohio, sewage
treatment plant with a diurnal periodic concentration change. Moment analy-
sis is used to discriminate between reversible adsorption in the sediments
and the irreversible precipitation or microbial utilization in the sediments.
The parameters for the irreversible model are calculated. These include the
reaction rate constant and the dispersion in the river.

Introduction

The principle of conservation of mass has been employed to model the concentrations of various substances in rivers since the initial work of Streeter and Phelps[1]. Their equation essentially was a mass balance on the dissolved oxygen in a stream. O'Conner[2] modified the equation to include the dispersion term and the resultant equation takes the form shown below.

$$D \frac{\partial^2 C_i}{\partial X^2} - V \frac{\partial C_i}{\partial X} - \frac{\partial C_i}{\partial t} - \sum_{i=1}^{n} k_i C_i = 0 \qquad (1)$$

where C_i = concentration of ith chemical species
X = distance downstream
t = time
D = dispersion coefficient
v = average stream velocity
k_i = rate constant for i^{th} reaction

This equation has been used to model the fate of metals and radioactive substances e.g., (Rohatgi and Chen[3]). The goal of the work was to predict the ultimate fate of the materials if a spill should occur in a stream. Willis, et al.[4], discuss the mass balance modeling of various substances for water quality prediction. Again, the goal is to predict the water quality under changing pollutant loads. The influence of convection and dispersion on the dilution of a substance in perennial streams has been also studied using this type of equation.

All of these studies use the same methodology for applying the conservation of mass to streams. First, the parameters of the model such as the dispersion coefficient, the average water velocity, and the kinetic coefficients are estimated. The analytical or numerical solution to the equations is then obtained. The predictions of the model are compared with the measured data.

If the comparison is not good, the parameters are modified until the fit is as "close" as can be achieved. This is called the calibration of the model. Following the calibration, the model is used to predict concentrations in the stream under somewhat different conditions and the model is again compared with the experimental data for this new condition. If the model compares well with the data under these new conditions, the model is considered to be verified. A verified mass balance model then can be used to predict the conditions of the river under various loading and weather conditions which do not differ significantly from the conditions used in the calibration. Such predictions are used in management situations to determine the best strategies to improve water quality or to minimize hazard.

The major problem with this modeling procedure is the estimation of the parameters. Usually, the estimation of the parameter values, or equivalently the calibration of the model, takes several iterations in which the predicted results are compared with the field data. To optimize the parameter values in any sense usually requires a rather elaborate computer algorithm and considerable computation time.

This paper presents a different approach for the estimation of parameters and further suggests that the mass balance equation (Equation 1) can be used with data to compare different mechanisms for concentration change. The procedure is to use natural or artificial time varying inputs into the stream along with moment analysis derived from the conservation equations to estimate constants and compare mechanisms. The particular application to be discussed in this paper involves the transport and reactions of phosphorus downstream from a municipal outfall. The time variation in this instance is the natural diurnal oscillation of phosphate concentration from a sewage treatment plant.

Literature Review

Measurements downstream from a sewage treatment outfall have been made innumerable times but in most cases the prime variables of interest have been dissolved oxygen and BOD. The measurements of ortho or total phosphorus downstream are not that extensive. However, there have been enough measurements to indicate what the dynamics of phosphorus might be.

It has been thought for some time that total and ortho phosphorus is removed from the water column during low flow conditions and carried out of the watershed during high flow events. This idea was suggested by Keup[5] primarily as an explanation for the increasing total phosphorus concentrations with increasing flows. Connell[6] also observed a significant removal of total phosphorus during low flows and a subsequent increase in total phosphorus concentration at the beginning of a storm event. McKee et al.[7] has measured significant nutrient concentrations in river sediments. Thus, it might be concluded that during low flows the ortho phosphorus is removed from the water column and accumulated in the sediments. The mechanisms by which this occurs might be adsorption on clay particles or accumulation by microorganisms.

The understanding of the phosphorus removal process is complicated by the diurnal variations in the phosphorus concentrations. This diurnal variation could be caused by the input of sewage treatment plants as shown in this paper or it could have other origins such as discussed by Cahill et al.[8]. There are other documentations of this temperal oscillation. Thus, if one wishes to use Equation 1 to estimate the first order rate constant for the disappearance of phosphorus in a given reach of stream from measurements at both ends of the reach one must contend with the oscillations. Since the oscillations are not approximated by any function, estimation procedures would involve numerical simulations and comparisons.

However, these temperal variations suggest a very easy method of analysis, i.e., the method of moments. The municipal sewage treatment plant creates an input of phosphorus concentration which resembles a probability distribution in time. It is possible to calculate the temporal moments of this distribution at both the upstream station and the downstream station. The change in moments between the two stations is related to the parameters in Equation 1 by the method of moments.

The method of moments has been used for years to determine the dispersion coefficient in tubes as presented by Aris[9]. Some of this methodology has been applied to rivers to determine the dispersion coefficient therein (see for example Parker[10]). The most recent research on dispersion coefficient measurement has concentrated on the initial development of the moments from given injection conditions and on the time to reach the normal distribution of concentration after the dye injection. However, there has been little investigation in which the method of moments has been used to estimate kinetic parameters in a stream.

The basic concepts for the use of the method of moments for the simultaneous estimation of dispersion coefficients and kinetic constants have been developed by workers in the area of chromatography. The equation describing the mass balance processes in a chromatograph are exactly the same as those for a river, e.g., the equations for chromatography are equivalent to Equation 1. Yamaoka and Nakagawa 11-13 in a series of papers discuss the application of the method of moments to a set of equations similar to Equation 1. They present the mathematical details of the process, but they do not investigate the details of the actual application to experimental chromatograms. In particular, they do not attempt to use the various methods for numerically calculating moments from the experimental data nor do they discuss the sensitivity of parameter estimation.

Theoretical Development

There are various models that can be attempted for understanding the dispersion and reaction of ortho phosphorus downstream from a municipal sewage treatment plant. These models all differ in the form of the reaction term in the equation. Sometimes these models entail another differential equation but always the equations are linear or approximated by linear functions such that the Laplace Transform can be obtained. In this section, the mathematical derivations will be obtained for two different models which could possibly describe the ortho phosphorus dynamics.

The first model to be considered involves the adsorption and desorption of ortho phosphorus from the sediments. The equations which describe the dynamics in this situation are listed below.

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial X} - D \frac{\partial^2 C}{\partial X^2} + k (C-C_s) = 0 \tag{2}$$

$$m \frac{\partial C_s}{\partial t} = k (C-C_s) \tag{3}$$

where C_s = concentration of ortho phosphate in the water adjacent to river sediments

k = mass transfer coefficient

m = adsorption capability of sediments

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This model essentially assumes that the rate of adsorption and desorption of ortho phosphorus to the sediments is mass transfer limited.

The boundary conditions associated with these equations then are determined by the input from the sewage plant, which is a diurnal oscillatory function with the rise in concentration occurring in the afternoon. This input then is a sequence of normal-shaped curves. Since the model is linear, each one of these normal-shaped curves can be considered separately. The total output can be obtained by summing the output of each normal curve. The boundary conditions associated with the passage of each normal-shaped curve is as follows.

$$@ \ t = 0 \quad C = C_s = 0 \tag{4}$$

$$@ \ X = 0 \quad C = C_o(t) \tag{5}$$

$$@ \ X = L \quad \frac{dC}{ds} = 0 \tag{6}$$

where L = distance between sample points in stream
$C_o(t)$ = ortho phosphorus concentration in the stream as caused by an afternoon input from a plant

The following dimensionless variables are defined.

$$\varepsilon = X/L \qquad \Theta = vt/L \qquad R = d/L \tag{7}$$

$$Pe = vd/D = \text{Peclet Number}$$

$$Th = d\sqrt{k/D} = \text{Thiele Modulus}$$

$$Am = \frac{mv}{kd}$$

where d = characteristic length e.g., river wetted perimeter.

Substituting these quantities into the equation then yields the following.

$$\frac{\partial C}{\partial \Theta} + \frac{\partial C}{\partial \varepsilon} - \frac{R}{Pe} \frac{\partial^2 C}{\partial \varepsilon^2} + \frac{Th^2}{PeR}(C - C_s) = 0 \tag{8}$$

$$Am \frac{\partial C_s}{\partial \Theta} = (C - C_s) \tag{9}$$

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There really are three parameters to be determined from these equations;

Am, $A = R/Pe$, and $B = Th^2/PeR$.

The second model to be considered is simpler than the first in that phosphorus is presumed to disappear from the stream by a first order kinetics. This model would correspond to such phenomena as microbial uptake. The equation for this case is given below.

$$\frac{\partial C}{\partial t} + v\frac{\partial C}{\partial X} - D\frac{\partial^2 C}{\partial X^2} + kC = 0 \tag{10}$$

The boundary conditions given by Equations 4, 5 and 6 apply here also.

Using the same dimensionless variables, this equation can be written thus.

$$\frac{\partial C}{\partial \Theta} + \frac{\partial C}{\partial \epsilon} - A\frac{\partial^2 C}{\partial \epsilon^2} + BC = 0 \tag{11}$$

In this equation, there are two parameters to be determined; A and B. This in effect will determine the Peclet Number and a Thiele Modulus.

Method of Moments

The goal of the analysis is to obtain parameters A, B and Am for Equations 8 and 9 or to evaluate parameters A and B of Equation 11. These numbers are to be estimated from experimental concentration measurements at the beginning and end of the stream reach of interest by the method of moments.

A good description of the mathematical procedures to be sketched here is given by J.M. Douglas [14]. The mathematics will be derived for the simpler model (Equation 11) and the results will be stated for the more complicated model (Equations 8 and 9).

First, the Laplace transform is taken of Equation 11 using boundary condition (Equation 4).

$$s\widetilde{C} + \frac{d\widetilde{C}}{d\epsilon} - A\frac{d^2\widetilde{C}}{d\epsilon^2} + B\widetilde{C} = 0 \tag{12}$$

where s = Laplace variable
C = concentration in Laplace domain

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This equation is integrated to obtain

$$\widetilde{C} = A_1 \exp[(1/2 + M)\epsilon/A] + A_2 \exp[(1/2 - M)\epsilon/A] \qquad (13)$$

where $M = \sqrt{1/4 + B(s + A)}$

The boundary conditions (Equations 5 and 6) are used to evaluate constants A_1 and A_2. Equation 6 can be replaced with a more convenient condition. (see Friedly[15])

$$\epsilon \rightarrow \infty \qquad C \rightarrow 0 \qquad (14)$$

In the Laplace domain then the solution is

$$\widetilde{C} = \widetilde{C}_o \exp[(1/2 - M)\epsilon/A] \qquad (15)$$

where $\widetilde{C}_o$ = Laplace transform of $C_o(t)$

Evaluate the function at $\epsilon = 1$ ($X = L$) and obtains a relationship between the Laplace tranform of the concentration at each end of the river reach.

$$\widetilde{C}_1 = \widetilde{C}_o \exp[(1/2 - M)/A] = H(s) \qquad (16)$$

The method of moments is based upon the expansion of the Laplace transformed concentration functions into the series of moments.

$$\widetilde{C}_o = \sum_{j=0}^{\infty} (-1)^j \frac{s^j}{j!} M_{0j} \qquad (17)$$

$$\widetilde{C}_1 = \sum_{j=0}^{\infty} (-1)^j \frac{s^j}{j!} M_{1j} \qquad (18)$$

where M_{0j} = j^{th} time moment of the function at $\epsilon = 0$
M_{1j} = j^{th} time moment of the function at $\epsilon = 1$

These moments can be evaluated from the experimental data. Also, $H(s)$ can be expanded in a Taylor series.

$$H(s) = H(0) + \frac{\partial H}{\partial s} s + \frac{1}{2} \frac{\partial^2 H}{\partial s^2} s^2 + \cdots \cdots \tag{19}$$

The following equations are derived by equating powers of s when equations 17, 18, and 19 are substituted into Equation 16.

$$\frac{M_{10}}{M_{00}} = \exp\left(\left[\frac{1}{2} - (AB + \frac{1}{4})^{1/4}\right] \frac{1}{A}\right) = A_H \tag{20}$$

$$\frac{M_{01}}{M_{00}} - \frac{M_{11}}{M_{10}} = -\frac{1}{2}(AB + \frac{1}{4})^{-1/2} = M_1 \tag{21}$$

$$\frac{M_{12}}{M_{10}} - \left(\frac{M_{11}}{M_{10}}\right)^2 - \frac{M_{02}}{M_{00}} + \left(\frac{M_{01}}{M_{00}}\right)^2 =$$

$$\sigma_1^2 - \sigma_0^2 = \frac{A}{4}(AB + \frac{1}{4})^{-3/2} = M_2 - M_1^2 \tag{22}$$

where σ_i^2 is the time variance of the concentration profile.

At $\epsilon = 0$, $\sigma_i^2 = \sigma_0^2$, and at $\epsilon = 1$, $\sigma_i^2 = \sigma_1^2$.

The equations can be used to solve for A and B given moments that are measured.

The same process can be applied to Equations 8 and 9 associated with the adsorption model. The resulting moment equations are as follows.

$$\frac{M_{10}}{M_{00}} = 1 \tag{23}$$

$$\frac{M_{01}}{M_{00}} - \frac{M_{11}}{M_{10}} = -(1 + A_m B) \tag{24}$$

$$\sigma_1^2 - \sigma_0^2 = 2A(1 + A_m B)^2 \tag{25}$$

These equations then could, in principle, be used to obtain A and $A_m \times B$ from experimental measurements of moments. Higher moments are required to solve A_m and B.

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Discussion of Theoretical Results

A comparison of the zeroth moment of the adsorption model with that of the reaction model indicates a significant difference. With the adsorption theory, there should be no change in the area under the curve, whereas the reaction theory indicates a decreasing area as the phosphorus progresses downstream.

Figure 1 contains a plot of A_H as a function of the reciprocal of B with the reciprocal of A as the parameter. As can be seen from the graph, the value of A_H primarily depends upon the value of the B parameter and thus the changing area of the curves can be used to evaluate B. In fact, Figure 1 will be used for the determination of the first order rate constant for the example included in this paper.

The reaction model with the parameter B equal to zero corresponds to the case of only dye dispersion with no reaction in a stream and under this circumstance A_H equals to one which is exactly equivalent to the ratio of zeroth moments for the adsorption model. Thus, adsorption model and the case of pure dispersion with no reaction cannot be distinguished using the zeroth moments. Any change in the zeroth moment indicates an irreversible reaction in the stream.

Equations 21 and 24 express the relationship of the first moment of the concentration profile as it moves downstream. This first moment is the average time of travel. Under conditions of no reaction or no adsorption, the average dimensionless time of travel, M_1, is equal to the average time of travel for the water itself, i.e., with either adsorption or reaction occurring, the average time of travel is increased. It is interesting to note that the dispersion does affect the time of travel for the case of reaction but not for the case of adsorption.

The value of the first moment, M_1, is plotted in Figure 2 as a function of the reciprocal of B with the reciprocal of A as a parameter (Equation 21). It can be seen that both the parameters A and B have the same influence since the first moment involves the product of the two. It should be noted that 1/A equals L/D and when this quantity is small, significant error can result in the measurement of travel time even though there is only a minor reaction occurring, i.e., 1/B is large. In these instances, care should be exercised that the tracer for average water travel time measurements does not react in any way with sediment material.

Figure 3 contains a plot of the first moment, M_1, for the adsorption model as a function of the dimensionless adsorption isotherm equilibrium constant with the dimensionless mass transfer coefficient as a parameter. Again, the product of these two dimensionless variables is important. From the figure, it is apparent that in streams with high mass transfer coefficients (very shallow streams) even a low dimensionless equilibrium constant will cause deviations of the travel time for the dye as compared with the water. In these instances, average travel time measurements from dye tracers would not correspond to actual average travel time of the water.
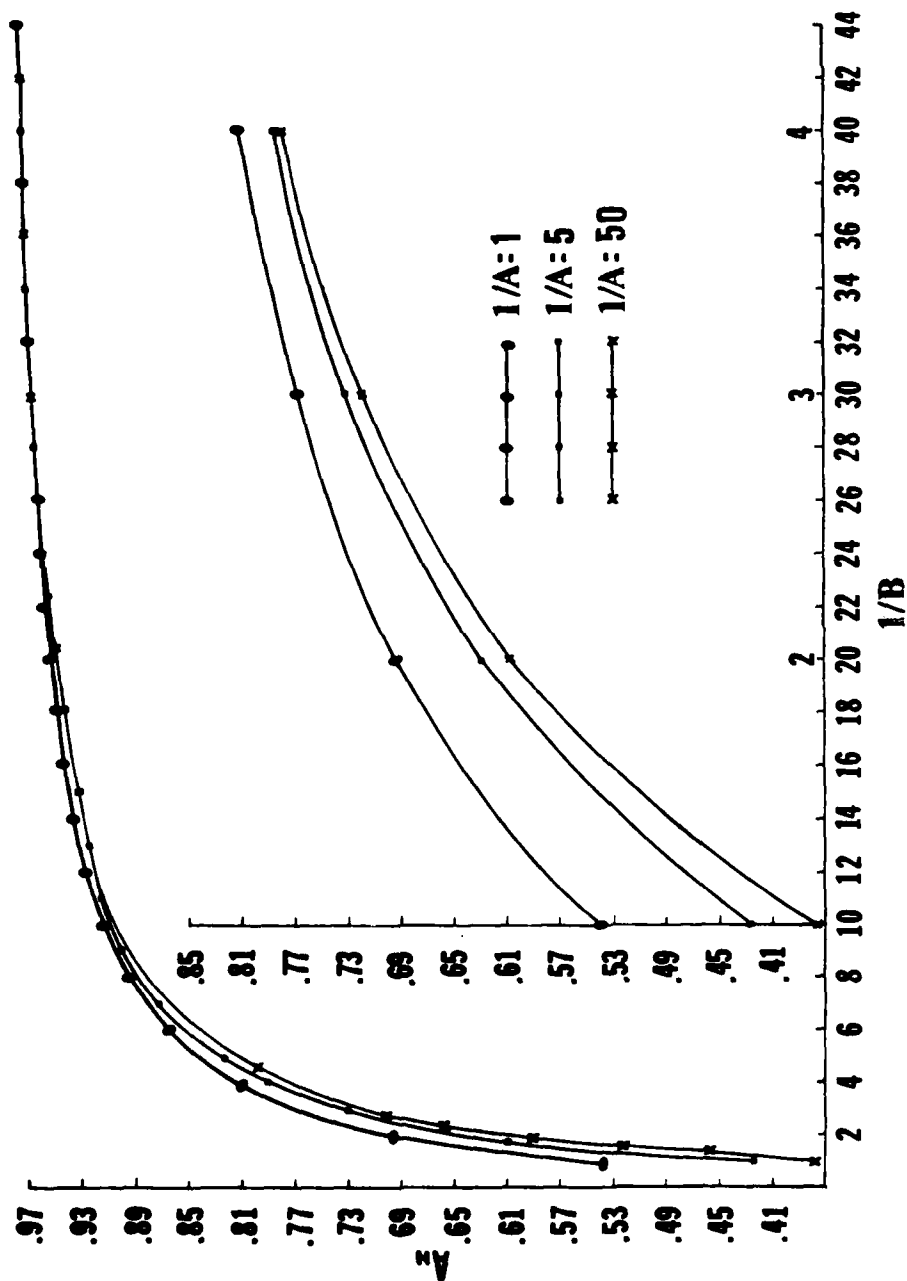
Figure 1. A plot of the Zeroth Moment Ratio, A_H, as a Function of the Reaction Parameter, 1/B, for Various Values of the Dispersion Parameter, 1/A.
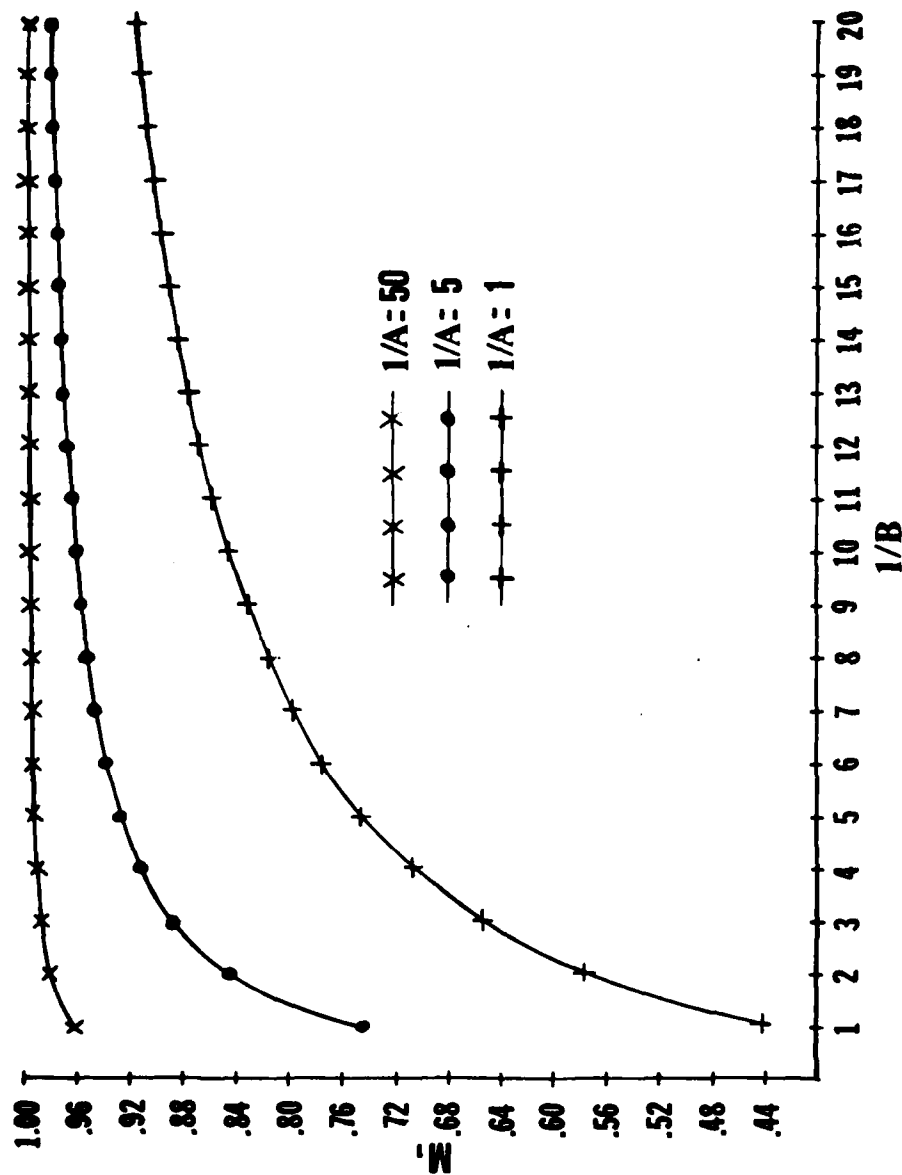
Figure 2. A Plot of the First Moment, M_1, as a Function of the Reaction Parameter, 1/B, for Various Values of the Dispersion Parameter, 1/A.
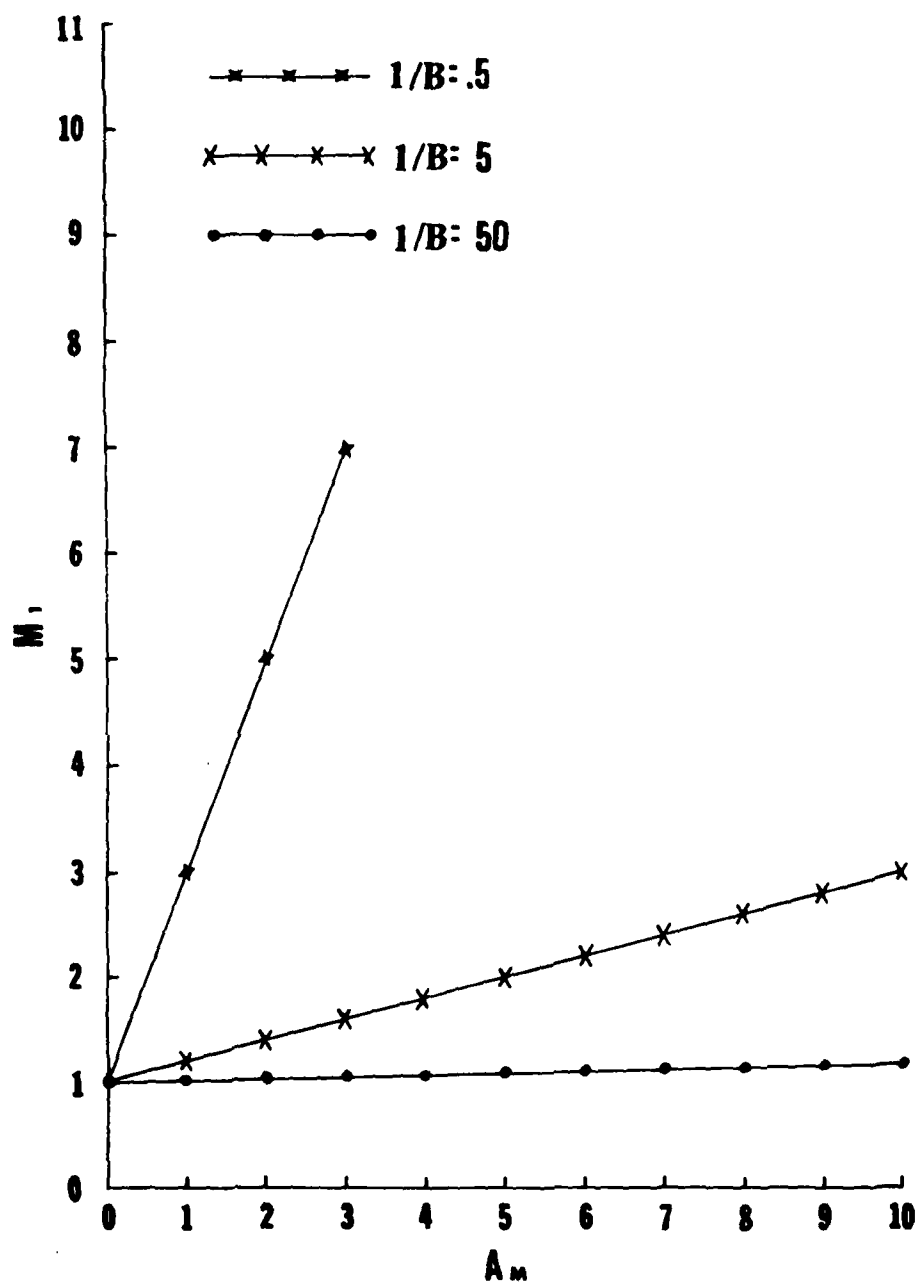
Figure 3. The Resulting Linear Plot of the First Moment, M_1, as a Function of the Adsorption Capacity Parameter, Am, for Various Values of the Reaction Parameter, 1/B.

The change of variance for the reaction model is shown in Figure 4 where it is plotted as a function of the dimensionless dispersion coefficient with the dimensionless reaction parameter coefficient as a parameter. For reasonably small values of the dimensionless dispersion parameter, A, the change in variance is primarily dependent upon this value with little dependence on the dimensionless reaction parameter. For very large values of the variable $1/B$, i.e., very little influence of the reaction, the variance function approaches that usually employed for measuring the dispersion coefficient.

The theoretical discussion has shown how the method of moments can be used to discriminate between different models. For the case of ortho phosphorus entering from a point source, two models were discussed. The zeroth moment can be used to distinguish between the two models since this moment will be decreased for the reaction model but it will remain the same for the adsorption model. The first moment for both models will indicate an average travel time for phosphorus to be larger than that of the water. The variance increases for both models but the dependency is quite different.

In addition to the discrimination between models, the method of moments can be used for the calculation of the dimensionless parameters in the models. For example, the reaction model involves two dimensionless coefficients, A and B, which can be estimated from the zeroth and first moment if necessary. Later it will be shown that the zeroth and the second moments are the best. On the other hand, the first, second, and third moments are required to estimate the three parameters of the adsorption model, A, B, and Am. The zeroth moment gives no information concerning the value of these parameter, thus further moments are required.

Data From the Sandusky River in Ohio

Bucyrus, Ohio, located on the upper reaches of the Sandusky River, operates a municipal sewage treatment plant which does not have tertiary treatment for the removal of phosphorus. Samples taken at three stations are reported here: Kestetler (0.9 km from outfall), Denzer (4.25 km from outfall), and Mt. Zion (6.53 km from outfall). Samples were taken at one-hour intervals over a five-day period in November 1977. The river flow was low and approximately steady during the measurements. A dye dump was used to measure the water velocity and to serve as a marker for the traveling phosphorus peaks. After the samples were collected, they were stored under refrigeration for at most two days before they were analyzed. Autoanalyzer procedures were used to determine ortho phosphorus, total phosphorus, as well as other parameters. In addition, the conductivity was measured for each sample and the pH was determined intermittently. The dye concentrations from the dye dump were measured with a flourimeter. Since the ortho phosphorus is the primary variable of interest and since about three-fourths of the total phosphorus is ortho phosphorus, the modeling effort discussed in this paper will be on ortho phosphorus.

Figures 5, 6 and 7 contain the ortho phosphorus and dye concentrations as a function of time for the Kestetler, Denzer, and Mt. Zion stations, respectively. The diurnal nature ortho phosphorus concentration is obvious from these figures. As the water peaks proceed downstream from Kestetler to
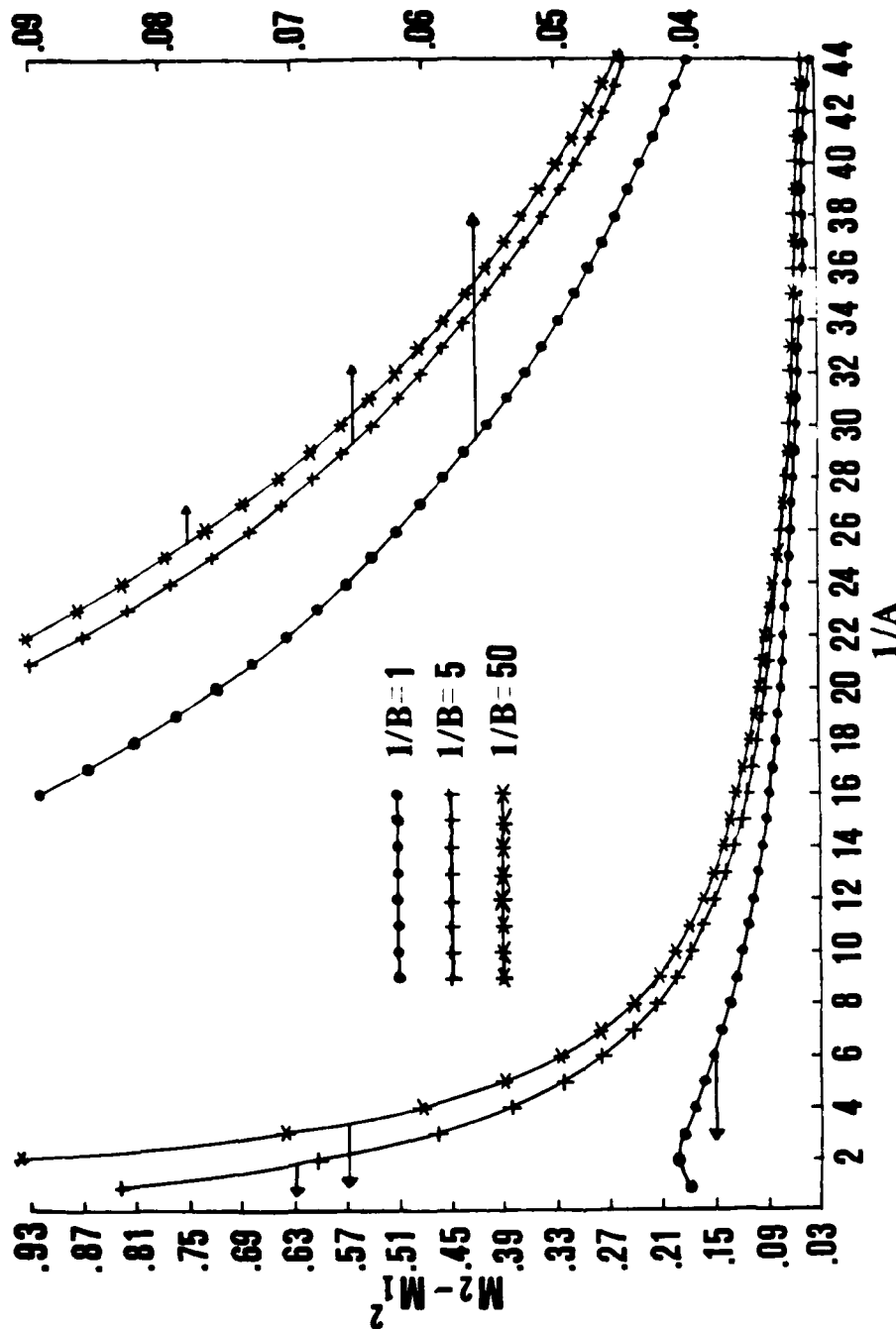
Figure 4. Dependency of the Second Moment on the Dispersion Parameter, 1/A, for Various Values of the Reaction Parameter, 1/B.
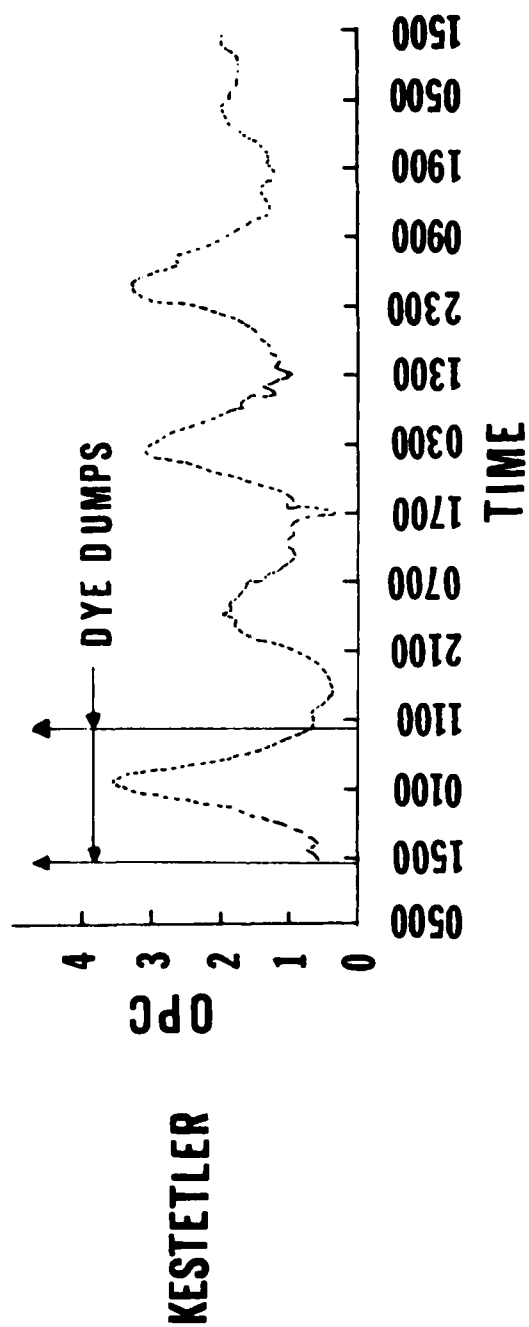
78

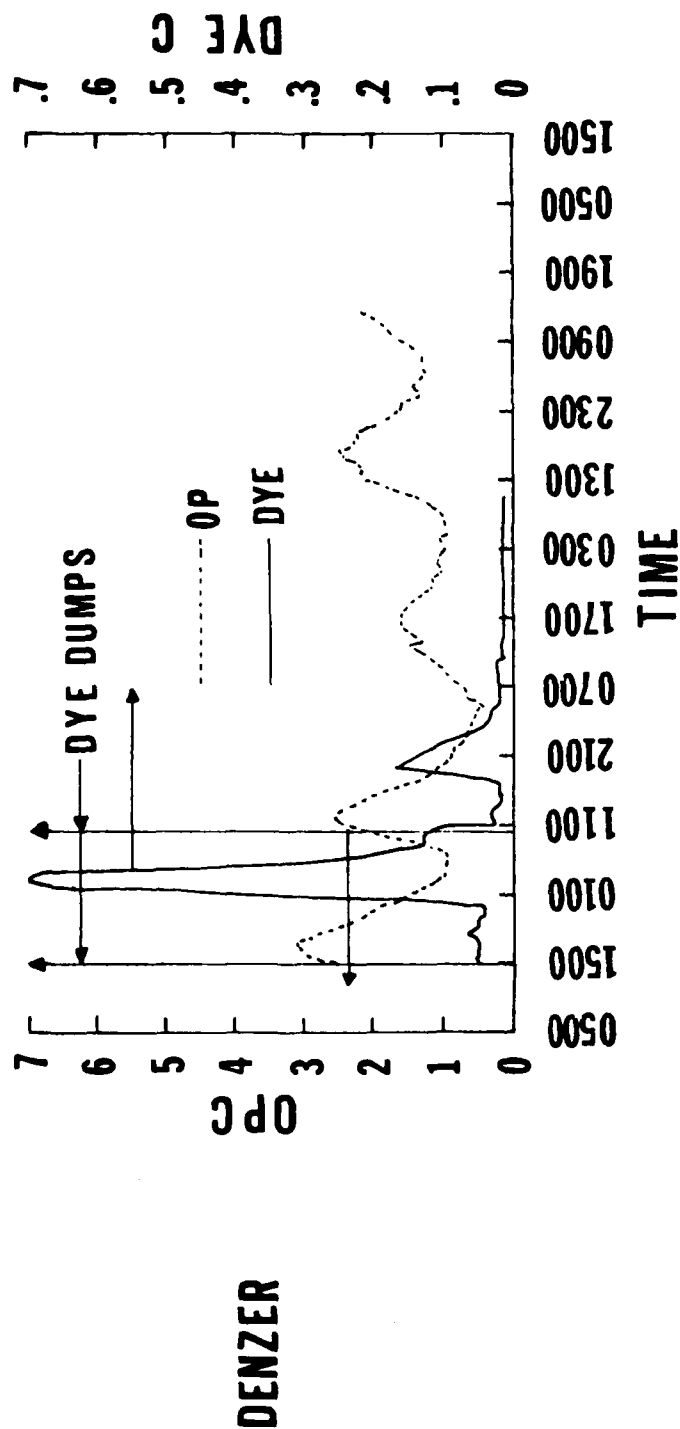Figure 5. Ortho Phosphorus Concentrations and Dye Dumps as a Function of Time at the Kestetler Station.

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Figure 6. Ortho Phosphorus and Dye Concentrations as a Function of Time at the Denzer Station.
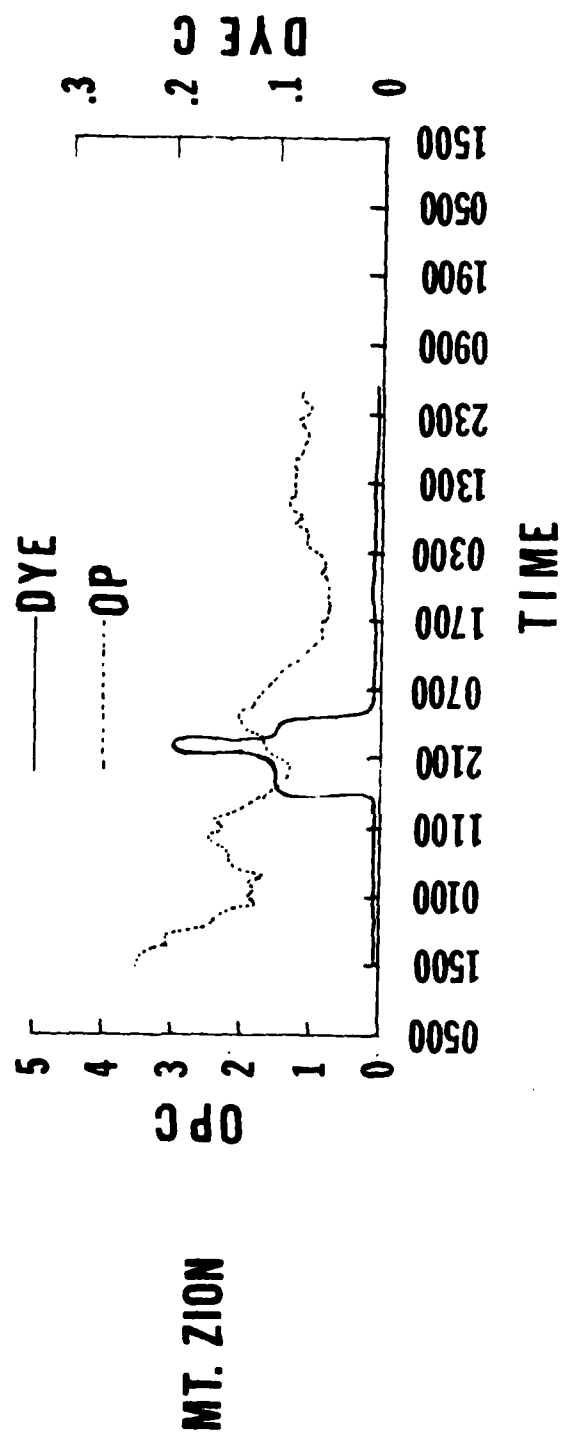
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Figure 7. Ortho Phosphorus and Dye Concentrations as a Function of Time for the Mt. Zion Station.

Mt. Zion, the dispersive activity spreads the peaks and flattens them out. The analysis to follow will determine if an adsorptive or a reaction phenomena is operative.

Calculation of the Moments From Experimental Data

An important aspect for the use of the method of moments are the procedure by which the moments of the experimental data is determined. Since the method of moments is following the movement of a single ortho phosphorus peak as it travels downstream, the moments must be calculated at each station for this peak neglecting the influence of other peaks. Three different schemes were attempted herein. The first scheme involved hand sketches of the tails of the ortho phosphorus peaks at each of the stations. This was unsuccessful because the higher moments of the curves were very sensitive to the assumed shape of the tail. From this it was concluded that the moment information wuld have to come from the middle portion of the ortho phosphorus peak, i.e., during the time when the ortho phosphorus concentration was elevated.

Since the estimation procedures must be based upon the central portion of the ortho phosphorus peak yet the higher moments are very dependent upon the tails of the functions, some equation must be assumed to reasonably represent the ortho phosphorus peak. For this analysis, the ortho phosphorus concentration as a function of time will be assumed Gaussian. G.I. Taylor[16] has shown experimentally and theoretically that a dye dump should become approximately Gaussian at a distance far enough downstream. Holley and Tsai[17] discuss what is meant by far enough.

The first procedure employing the Gaussian function was to use the peak value and its associated time along with the one-half peak values and their associated time values. This method provided to be better than the curve sketching procedure; however, it was very sensitive to errors in the measurement of the peak ortho phosphorus concentration. The third and best method for the estimation of the moments was to fit the central portion of the curve to a Gaussian function using a transformation and linear least squares. For linear least squares, the Gaussian formula can be written in the following form.

$$\ln(c) = at^2 + bt + c \tag{27}$$

where a, b, and c are constants
and ln = natural logarithm

Figure 8 shows an excellent correspondence between the least square Gaussian curve and the experimental data for a ortho phosphorus concentration peak at Kestetler. Also shown on this figure is a poorer fit to data taken at Denzer. Considering the experimental error in the measurements, all of the data followed a Gaussian function reasonably well.

The following formulas are used to calculate the moments from the coefficients a, b, and c determined by the least squares.

$$\sigma^2 = \frac{M_2}{M_0} - \left(\frac{M_1}{M_0}\right)^2 = \frac{1}{2a} \tag{28}$$
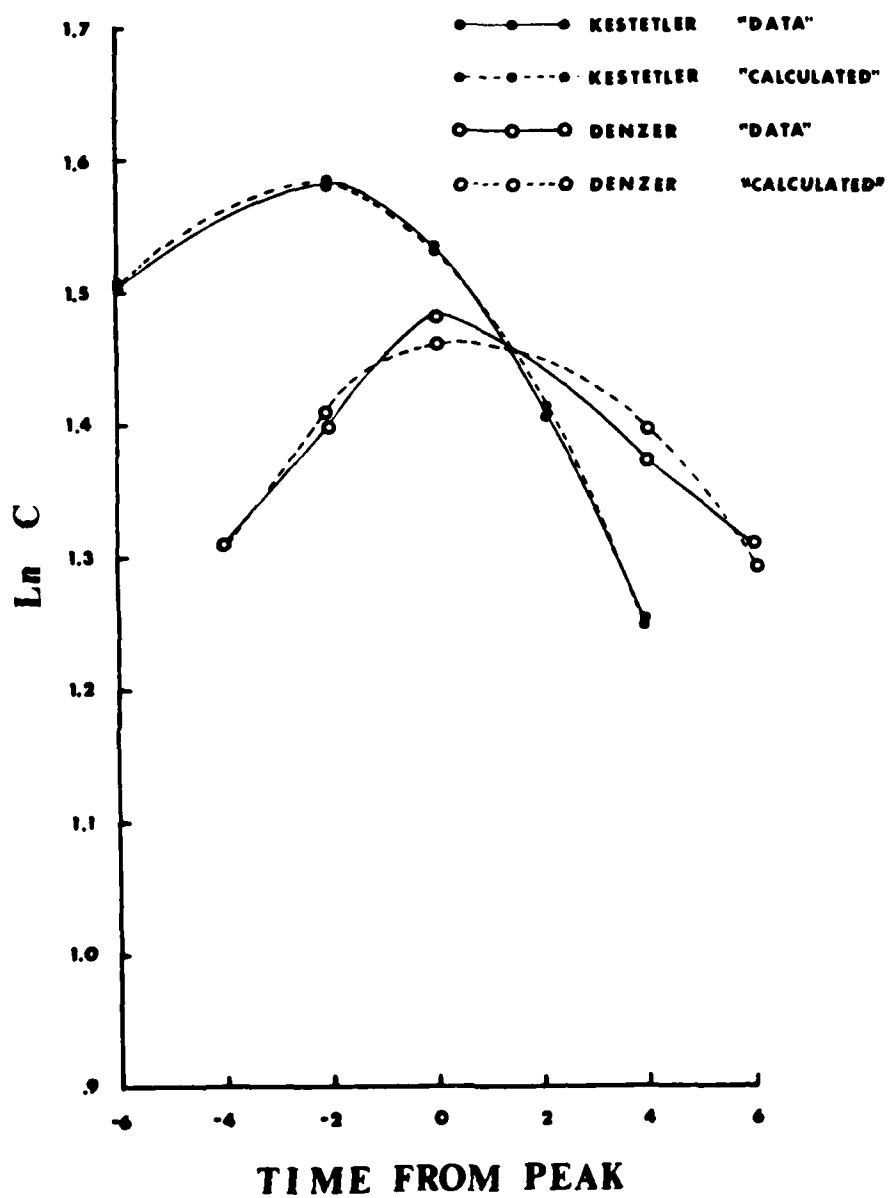
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Figure 8. Examples of the Least Squares Fitting of the Ortho
Phosphorus Concentration to a Normal Distribution Function at
Kestetler and Denzer.

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$$\mu = \frac{M_1}{M_0} = \frac{b}{2a} \tag{29}$$

$$c = \ln \frac{M_0}{\sqrt{2\pi}\ \sigma} - \frac{\mu^2}{2\sigma^2} \tag{30}$$

Model Discrimination and Parameter Estimation for Sandusky River

The two models to be tested are the adsorption model and the reaction model developed previously. Two phosphorus peaks were followed from Kestetler to Denzer and on to Mt. Zion. The moments calculated for one of these peaks at each of the stations is listed in Table 1. The key moment for the discrimination between the two models is the zeroth moment. From Table 1 it is apparent that the zeroth moment decreases in value as the phosphorus peak proceeds downstream. Thus, the reaction model is favored over the adsorption model. This implies that the ortho phosphorus is removed from the river water column by a mechanism other than equilibrium adsorption to clay particles in the stream. Three possible mechanisms to explain this reaction removal of ortho phosphorus are microbial uptake of the phosphorus from the water column, the reaction to form insoluble solids in the sediments, or the sedimentation of precipitated ortho phosphorus. The dimensionless reaction coefficient between Denzer and Mt. Zion is much lower than that between Kestetler and Denzer. If it were postulated that the major uptake of ortho phosphorus is via algal microbial activity, this difference could be explained by the time of day. The water parcel went from Kestetler to Denzer from early morning until early afternoon during which active uptake of ortho phosphorus would occur. The passage from Denzer to Mt. Zion occurred during late afternoon and night with less algal biological activity.

Table 1 - Moments for Phosphorus Peaks, November 1976 Data

	M_0	M_1	σ	μ
Kestetler	27.9	− 6.26	3.27	− 0.2
Denzer	24.2	254	3.80	10.5
Mt. Zion	23.9	592	4.70	24.7

It is also of interest to compare the dispersion coefficient for the two reaches. Table 2 indicates that the parameter A has a value of .0197 from Kestetler to Denzer and a value of .0362 from Denzer to Mt. Zion. The distance is approximately the same but the water velocity between Denzer and Mt. Zion was slower. The ratio of A values was nearly equal to the inverse ratio of velocities. Thus, the dispersion coefficient was nearly equal for the two reaches.

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Table 2 - Dispersion Coefficients

	$R/Pe = \dfrac{D}{VL}$	$Th^2 = \dfrac{kL}{PeR} \quad \dfrac{}{v}$
Kestetler to Denzer	.0197	.01348
Denzer to Mt. Zion	.03620	.0021

Conclusions

The method of moments can be used to analyze concentration data in river systems. This analysis can be applied to continually occurring oscillations in concentration such as that associated with ortho phosphorus from a sewage treatment plant. Or the analysis could be applied to an intentional dump of some material into a stream. The moment analysis can be used to discriminate between different competing models for the explanation of a phenomena. For the case of ortho phosphorus downstream from an outfall, it was concluded that the reaction model was consistent with the measurements of the moments, and the adsorption model was not consistent.

The method of moments can be used to quantify various parameters such as the dimensionless dispersion and reaction parameters in the reaction model. The calculated rate of disappearance of ortho phosphorus using the estimated parameter was consistent with the few experimental measurements made some distance downstream. The dispersion parameter was also estimated for the reach of stream.

Concerning the transport of phosphorus in streams, it is concluded that point source ortho phosphorus from upstream outfalls does not traverse directly downstream and into the receiving water body. Rather this ortho phosphorus is accumulated in the sediments downstream from the outfall. It is transported downstream by a following storm which suspends some of the bottom sediments and transports them some distance downstream.

The parameters A and B are to be estimated from the date using Equations 20, 21, and 22. This yields three equations and two unknowns. However, the variation of the first moment from one for this application is very small and the error in estimating the deviation from one is very large; thus it is of little use in the estimation procedure. The zeroth moment and the variance are used to estimate parameters A and B. The estimation procedure is accomplished quickly because the zeroth moment does not depend to a great extent upon the A parameter; thus a good estimate of the reaction parameter B, can be obtained from the zeroth moment. This parameter is then entered into the equation for the variance change and the A dispersion parameter, A, is calculated. A few iterations using this procedure yields satifactory estimates of the parameters A and B.

From the above analysis, it was concluded that the ortho phosphorus from the municipal outfall was removed from the water column as the water flowed

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downstream. From the estimate of the reaction rate parameter B, it is possible to estimate the distance downstream the water must move before most of the phosphorus has been removed. This calculation assumes that the rate of removal remains constant throughout the stream reach. The first order of reaction implies the following equation.

$$\frac{dC}{dt} = - k_c \tag{31}$$

This equation is converted to the following form.

$$\frac{dC}{d\epsilon} = - \frac{kL}{v} C \tag{32}$$

The dimensionless time constant in this equation is simply the parameter B, i.e. (33)

$$B = \frac{kL}{v}$$

Since the distance between Kestetler and Denzer is about 3.35 kilometers and a dimensionless distance of about 14 will correspond to about 90 percent removal, it is expected that this 90 percent removal would be achieved about 50 kilometers downstream, if the stream velocity remains constant. Actually, the velocity decreases and the phosphorus is removed more rapidly than distance. Measurements 16 km downstream indicate that more than three-fourths of the ortho phosphorus has been removed at this point which is consistent with the model.

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